

New Acid O/W Microemulsion Systems for Application in Carbonate Acidizing

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ABSTRACT

The recent oil discoveries in pre-salt carbonates located at Brazil's offshore are the most significant of the last decade. Nevertheless, developing these fields remains difficult. The process of matrix acidizing, despite being one of the oldest operations in the petroleum industry, also presents several challenges, such as the control of the calcium dissolution reaction. Despite the fact that microemulsion systems present high potential for application as retarded acid systems, few studies have been carried out involving this application in stimulation. This work investigates the application of new oil in water (O/W) microemulsified acid systems as retarded acidizing fluid. Two nonionic surfactants, ALK90 and RNX110 were tested. Sec-butanol was used as co-surfactant, kerosene and xylene as the oil phase. The systems were obtained and tested in a bath reactor to evaluate the retarded in the calcium carbonate dissolution reaction. Coreflood experiments were carried out to evaluate the effectiveness to stimulate the core plugs and to form conductive channels, called wormholes. The results showed that O/W acid microemulsion systems were effective in retarding the dissolution reaction rate of the CaCO_3 being less corrosive than regular HCl solutions. Coreflood experiments confirmed the ability of the systems obtained to form wormholes and stimulate carbonate formations. The studies indicate that the systems have the potential to be used as retarded acid systems.

Key words: carbonate acidizing, microemulsion, dissolution, wormhole, retarded reaction.

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INTRODUCTION

Acidizing is a method of well stimulation widely used in the petroleum industry, involves pump an acid solution into the formation under fracture pressure. The main objective of acidizing is to stimulate the formation, increasing or restoring the permeability of the near

wellbore region. In carbonate formations, the mechanism that allows the increase in permeability is the dissolution of the rock caused by the reaction between the carbonate and the hydrochloric acid (HCl). The dissolution process forms conductive flow channels called “wormholes” that facilitate the flow through the near wellbore region, increasing the well production or injectivity [1]. Carbonate rocks are found in Calcite (CaCO_3) and Dolomite ($\text{CaMg}(\text{CO}_3)_2$) forms, the reactions with the HCl are represented for two forms, respectively in the equations (1) and (2).



Due to the strong reaction between acid and carbonate, when the injection occurs at low flow rates most of the acid is consumed near the rock face, in these conditions the acid does not form the “wormholes” structures and cannot pass the damage area. In these cases, it is necessary to retard the acid dissolution reaction to avoid the rock face dissolution and assure formation of wormholes [2]. This scenario is quite common in low permeability formations where the flow rate is limited due to the operational pressure window.

Retarded acid systems, as gelled and emulsified acid, are typically used to obtain lower dissolution reaction rates. Micelle structure and viscosity effect hindering the diffusion process of the acid in media causing a retarded effect in the dissolution reaction. These effects in conjunction with an optimum placement, it allows the wormhole formation and deeper acid penetration [3 – 5]. In this context, microemulsion systems (MES) are self-assembled systems formed by a mix of surfactant, co-surfactant, oil, and water phase, where the droplets of one liquid are dispersed in an immiscible continuous phase [18]. Different from emulsions, they are thermodynamically stable and present low interfacial tension [19 – 22]. MES have been studied in a prolific range of applications in the petroleum industry [7, 8, 30 – 40]. A work using water in oil (W/O) microemulsion as a retarded acid system shows that the microemulsions obtained were effective in retarding the dissolution reaction, reducing the diffusion coefficient by two orders of magnitude compared with regular HCl solution [11]. Other studies show surfactant and correlated systems being used as retarded acid systems [23 – 29]. Despite the potential of microemulsion for application in stimulation, a few studies show these self-assembly systems as retarded acid systems.

This work explores a new O/W acid microemulsion system created for application in carbonate acidizing. In the systems studied, the main mechanism responsible for the reaction retardation are the film formed by microemulsion droplet at the rock surface and the droplet structure in the fluid that hinder the diffusional process.

For the dissolution reaction, the methodology developed aims to compare qualitatively the rate of reaction in different systems. Coreflood experiments were conducted to evaluate the efficiency of the systems to form wormholes and stimulate carbonate formations. This work aims to contribute to the development of alternate stimulation fluids for application in carbonate acidizing.

MATERIALS AND METHODS

Chemicals of MES and pseudo-ternary diagrams

To obtain the acid microemulsified systems (AMS), two ethoxylates non-ionic surfactants (S) were tested: ALK90 and RNX110. The term nonionic indicates that in the polar side of the amphiphilic molecule there are no charges, this group of surfactants was chosen for being less sensitive to acidity and salinity effects [12, 13]. The ethoxylation grade is 9 for

ALK90 and 11 for RNX110. The remaining constituents of MES were: butan-2-ol used as co-surfactant (C); xylene and kerosene as oil phase (OP), and HCl aqueous solutions with concentrations ranging from 15 to 36% w/w used as aqueous phase (AP).

The phase diagrams were built at room temperature ($25 \pm 1^\circ\text{C}$) using a pseudo-ternary system composed of acid solution as aqueous phase, oil phase, and a fixed C/S ratio of 0.5. Microemulsion regions were determined in the diagram, observing the titration of different components of the system until the formation of a translucent solution, according to Winsor's definition [15].

Corrosion test

To compare the corrosiveness of the AMS obtained, the copper strip test was performed according procedure ASTM D130 using a Kaehler equipment– model K39395 [16]. The test consisted of the immersion of a polished copper strip in 30 mL of sampled fluids, placed for 3 hours under controlled temperature of 100°C . At the end of the heating period, the copper strip was removed, washed, and the color and tarnish level assessed against the ASTM Copper Strip Corrosion Standard.

Droplet size determination

The medium droplet size in the AMS was determined by dynamic light scattering using Nanotrak NPA252 equipment. The particle size distribution was characterized by mean diameter. The analyses were carried out in duplicate and the medium value was used. The measures were conducted at room temperature ($25 \pm 1^\circ\text{C}$). The results represent the medium droplet size of disperse phase in the acid microemulsion systems

Dissolution of calcium carbonate experiments

A reactor was designed and constructed to evaluate qualitatively the dissolution of calcium carbonate behavior in HCl solution and acid microemulsified media. The reactor consists in a reaction cell connected with a vacuum pump and one recipient to the acid solution. Figure 1 shows the reactor components and accessories. Commercial calcium carbonate, with 98 to 100% of purity, was placed inside the reaction cell and the acid solutions were released from the recipient. Consumption of calcium carbonate was correlated with the pressure increase as a result of the production of CO_2 . A transducer recorded the pressure in the reaction cell.

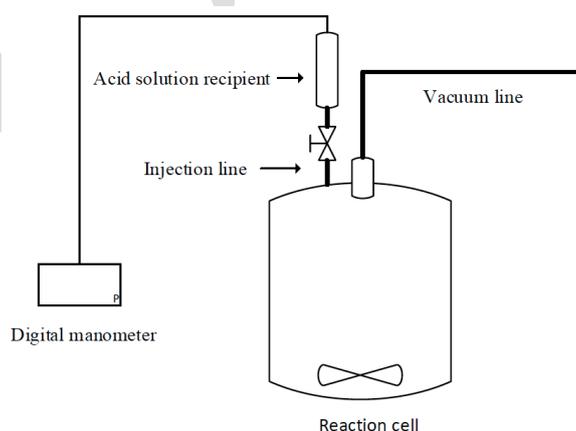


Fig 1: Schematic of reactor apparatus

Rheology of the microemulsified acid systems

The rheology for the acid microemulsified systems was determined with a Brookfield rheometer model R/S 2000, adapted with a water bath and a computer to record the data. The measure is based on dynamic coaxial cylinders immersed in the fluid sample with controlled shear rate. The shear rate range studied was $0 - 400\text{s}^{-1}$.

Coreflood experiments

In order to compare the efficiency of the acid systems studied, coreflood experiments were performed with the apparatus showed schematically in Figure 2. Fluid for injection was confined in the cell injection and injected axially through the rock core allocated in a core cell. The fluid was collected in the flow line and its volume was measured.

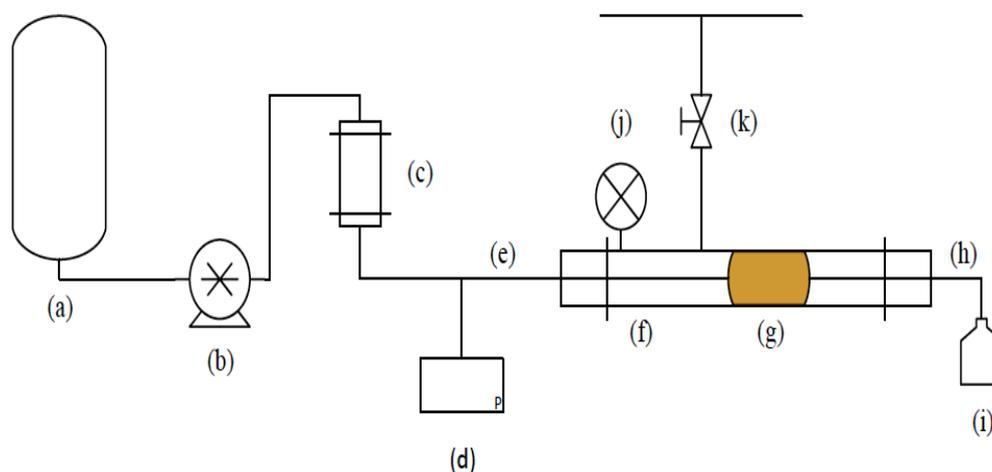


Fig 2: Coreflood setup: (a) water container; (b) pump; (c) fluid injection cell; (d) digital manometer; (e) injection line; (f) core cell; (g) rock core; (h) output line; (i) fluid collector; (j) pressure gauge; and (k) compressed air line

Carbonate coreplugs were prepared with 5.0 cm in diameter and 3.8 cm in length. Core samples used in these experiments were obtained from Jandaíra formation, located in the State of Rio Grande do Norte, northeast of Brazil. To assure that no fluids were trapped in the plug sample, minimizing the interference in the determination of porosity, they were calcined at 250°C , increasing the temperature gradually with rate of $10^{\circ}\text{C}/\text{min}$ [14]. The external area of the plugs was isolated with an epoxy resin, avoiding the radial flow, with the exception of the ends where acrylic diffusers were installed allowing a homogenous fluid injection.

The injection of the acid systems in the core was performed using the constant volumetric rate (CVR) method. Initially, 2% w/w of KCl brine was injected to saturate the plug and assure the complete filling of the pore space. The permeability was measured first by the acid treatment, using differential pressure across the core. One pore volume of the acid system was injected maintaining a constant flow rate. After the acid system injection in the plug a post-flush was performed with 2% of KCl brine, and the final permeability was measured. The pressure drop across the length of the core was monitored by a digital manometer and pressure gauge. Experiments were carried out at room temperature. Wormhole formations were evaluated by sectional cuts performed in the core.

RESULTS AND DISCUSSION

Microemulsionsystems

To determine which compositions allow the formation of microemulsion, it is necessary elucidate the phase behavior of the systems. The main propose, in this section, was to compare the surfactants (RNX110 and ALK90)and the oil components (kerosene and xylene) in the microemulsionformation (WIV). The pseudo ternary diagrams were obtained with the compositions presented in Table 1.

Table 1. System components for the phase diagrams

System	Surfactant	Co-surfactant	Oil phase	Aqueous phase
1	ALK90	Sec-butanol	Kerosene	HCl 15%
2	ALK90	Sec-butanol	Xylene	HCl 15%
3	RNX110	Sec-butanol	Kerosene	HCl 15%
4	RNX110	Sec-butanol	Xylene	HCl 15%

Figures 3 to 6 shows the phase diagrams obtained. This work focused on the use of O/W microemulsion(WIV) regions with less concentration of surfactant and high concentration of aqueous phase because they are more cost-effective. The systems used had a composition rich in aqueous component.

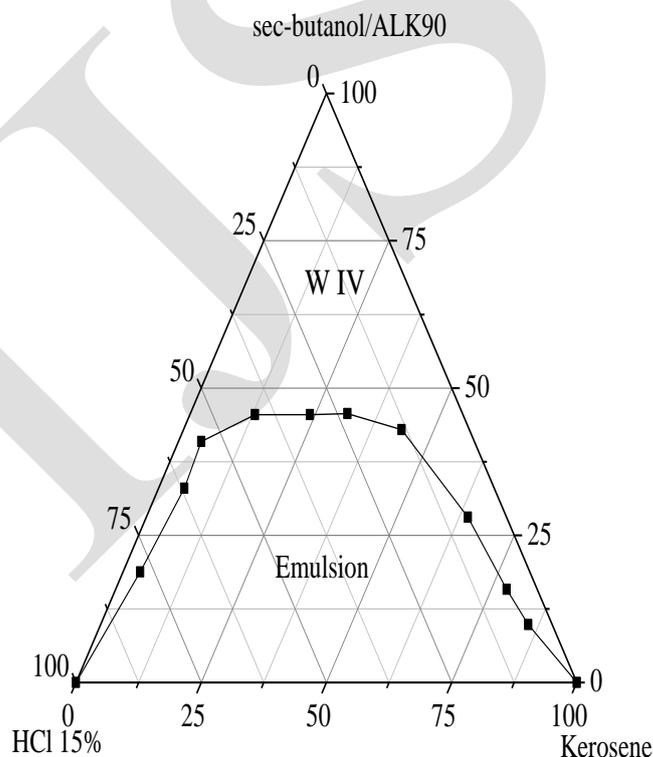


Fig 3: Phase diagram for system 1: ALK90 (S) +sec-butanol (C) + HCl solution 15% (w/w) + kerosene, with C/S=0,5at room temperature (25±1°C)

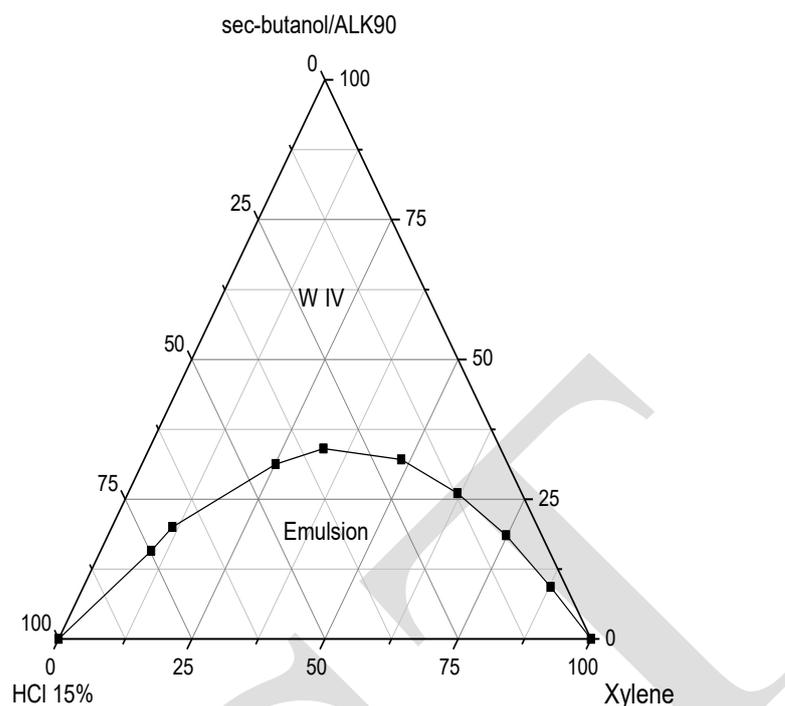


Fig4:Phase diagram for system 2: ALK90 (S) +sec-butanol (C) + HCl solution 15% (w/w) + xylene, with C/S=0,5 at room temperature ($25 \pm 1^\circ\text{C}$)

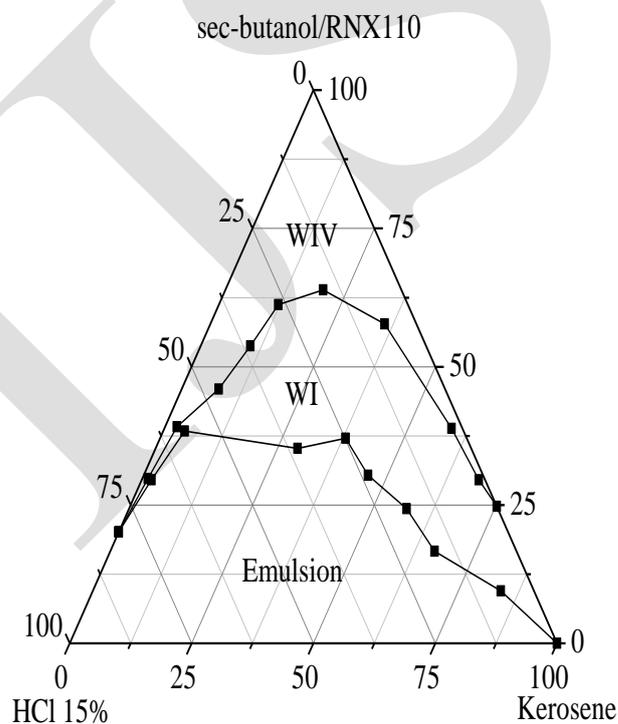


Fig 5: Phase diagram for system 3: RNX110 (S) +sec-butanol (C) + HCl solution 15% (w/w) + kerosene, with C/S=0,5 at room temperature ($25 \pm 1^\circ\text{C}$)

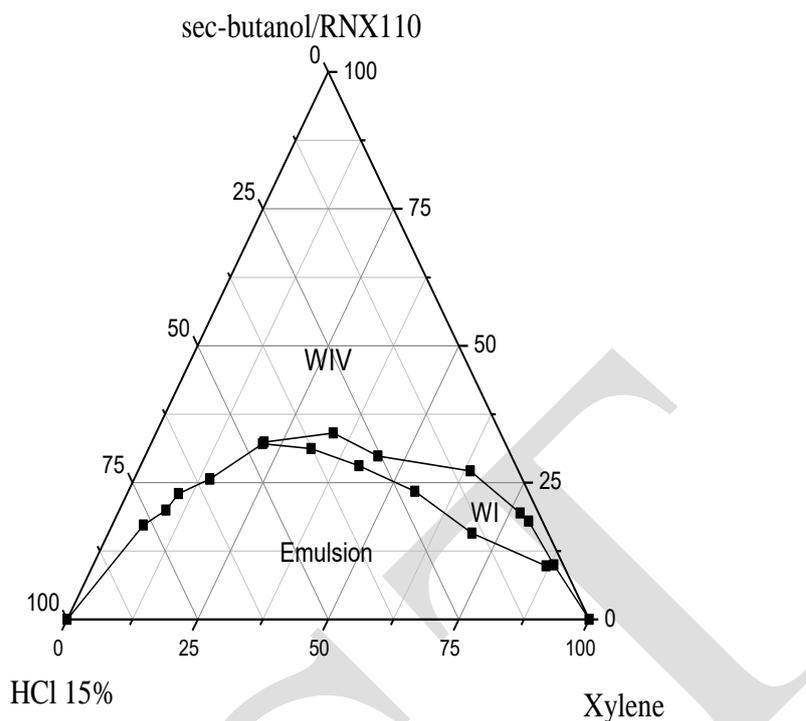


Fig 6: Phase diagram for system 4: RNX110 (S) +sec-butanol (C) + HCl solution 15% (w/w) + xylene, with C/S=0,5 at room temperature ($25 \pm 1^\circ\text{C}$)

The system 1, showed in Figure 3, presented a microemulsion region near the water vertex. The region was very narrow, making the system sensitive to small variations in composition. Stable microemulsion regions were found only with concentrations higher than 45% of co-surfactant/surfactant.

The diagrams of the systems with xylene as oil phase (systems 2 and 4) presented larger microemulsion regions, as one can see in Figures 4 and 6. These results indicate that xylene promotes an increased solubility of the systems studied, and microemulsions are closer to the region rich in aqueous phase.

In system 3 diagram, Figure 5, a WI (microemulsion in equilibrium with an oil phase) region was identified. However, stable microemulsion regions were formed only with co-surfactant/surfactant concentrations higher than 60%, what makes this system economically unfeasible. System 4 diagram, Figure 6, presented a microemulsion region similar to the one of system 2, but the surfactant RNX110 favors the formations of a WI region closer to the xylene vertex.

Corrosiveness test for microemulsified acid systems

Systems 1, 2, and 4 were evaluated concerning the performance of microemulsion systems to reduce the corrosiveness of HCl in solution. System 3 was not studied because it did not show WIV equilibrium in the region rich in aqueous phase. The total acid concentration in the systems studied varied from 15 to 18.3%, regular acid, normally used in acidizing jobs, has 15% HCl. Table 2 shows the corrosiveness results for the systems studies and the composition of each component. The corrosiveness varies from slight tarnish (1A to 1B) to corrosion (4A to 4C).

Table 2. Corrosiveness test results

#Test	System	Surfactant	%Co-surfactant	%Oil component	% Aqueous component	Total [HCl] %w/w	Corrosiveness Classification
1	1	23,3	11,7	2,5	62,5	16,3	1B
2	1	25,0	12,5	5,0	57,5	15,0	1B
3	2	23,3	11,7	2,5	62,5	16,3	2B
4	2	16,7	8,3	5,0	70,0	18,3	2C
5	2	20,0	10,0	5,0	65,0	17,0	2B
6	2	25,0	12,5	5,0	57,5	15,0	1B
7	4	25,0	12,5	5,0	57,5	15,0	1B
8	HCl 36%					36,0	4A
9	HCl 15%					15,0	2C

The results in Table 2 show that, although the total acid concentration was the same, the acid was less corrosive in the microemulsion than when in the aqueous solutions. Tests 2, 6, and 7 had 15% (w/w) of HCl and were classified as 1B. The HCl solution with the same acid concentration was classified as 2C in the corrosiveness grade. In system 2, the acid concentration was studied in the range of 15,0 to 18,3% (w/w) (tests 3, 4, 5, and 6), the results showed that the corrosiveness increased with the acid concentration. For 18,3% (w/w) of HCl microemulsified the corrosiveness was equivalent at the 15% w/w of HCl in aqueous solution, classified as 2C, indicating that the acid microemulsified is less corrosive than in aqueous solution. These results can be explained by two main mechanisms. The first mechanism is the droplet structure of the microemulsion, which, dispersed in the continuous phase, hinders the acid diffusion process, retarding the acid attack. The second, it is that the microemulsion forms a film that protects the metallic surfaces acting as corrosion inhibitor [41, 44]. This behavior also indicates that less corrosion inhibitor needs to be added to the microemulsified acid systems if compared to the aqueous HCl solution.

Table 3. Particle size results

System	Surfactant	Co-surfactant	Oil component	Aqueous component	[HCl] % w/w	Particle size (nm)
1	23,3	11,7	2,5	62,5	16,3	81,7
2	16,7	8,3	5,0	70,0	18,3	133,0
2	23,3	11,7	2,5	62,5	16,3	90,6
2	25,0	12,5	5,0	57,5	15,0	80,3
4	16,7	8,3	5,0	70,0	18,3	183,4
4	23,3	11,7	2,5	62,5	16,3	180,0
4	25,0	12,5	5,0	57,5	15,0	158,0

Particle size diameter of the microemulsified acid systems

Table 3 shows the mean droplet diameter obtained for each microemulsified acid system. The results showed that for the surfactant ALK90 the mean diameter varied from 80 to 133 nm and for the RNX 110 the mean droplet diameter varied from 158 to 183 nm. These results indicate that ALK90 favors the formation of smaller droplets, which enhance the surface area between dispersed and continuous phases. For both systems, the increase in surfactant concentration reduced the droplet diameter. This behavior is due to the increase in surfactant concentration, which favors the stability of the microemulsion systems. Therefore,

with lower surfactant concentrations, the system is prone to form emulsions, nanoemulsions, or other non-self-assembled structures. These kinds of structures need additional energy to maintain the system miscible and are susceptible to coalescence, creaming and flocculation effects [42, 43].

Dissolution of calcium carbonate in microemulsified acid media

Systems 2, 4, and HCl 15% were tested in order to evaluate qualitatively the rate of dissolution of the calcium carbonate. As observed in Figure 7, the dissolution of the CaCO_3 in the solution of HCl 15% occurred rapidly, within 55 seconds approximately 98% of the calcium carbonate was consumed. The microemulsified acid takes more time to react with the calcium carbonate (red and green lines). The systems 2 and 4 reach more than 90% of conversion at 1413 and 396 seconds, respectively. The maximum conversions achieved in the experiments were 98% by the acid in HCl 15%, and 95% for the acid in microemulsified systems 2 and 4. The results indicate that system 2 was more effective in retarding the dissolution reaction of the calcium carbonate in acid. The results showed that when the acid is in the microemulsion media the dissolution process is slower than in aqueous media. It is important to understand that in O/W microemulsions the acid is mainly in the continuous phase and some acid is in the interface. Thereafter, the mechanism of retard is different of W/O microemulsion found in other studies where the acid is confined in the droplet structure [11, 45, 46].

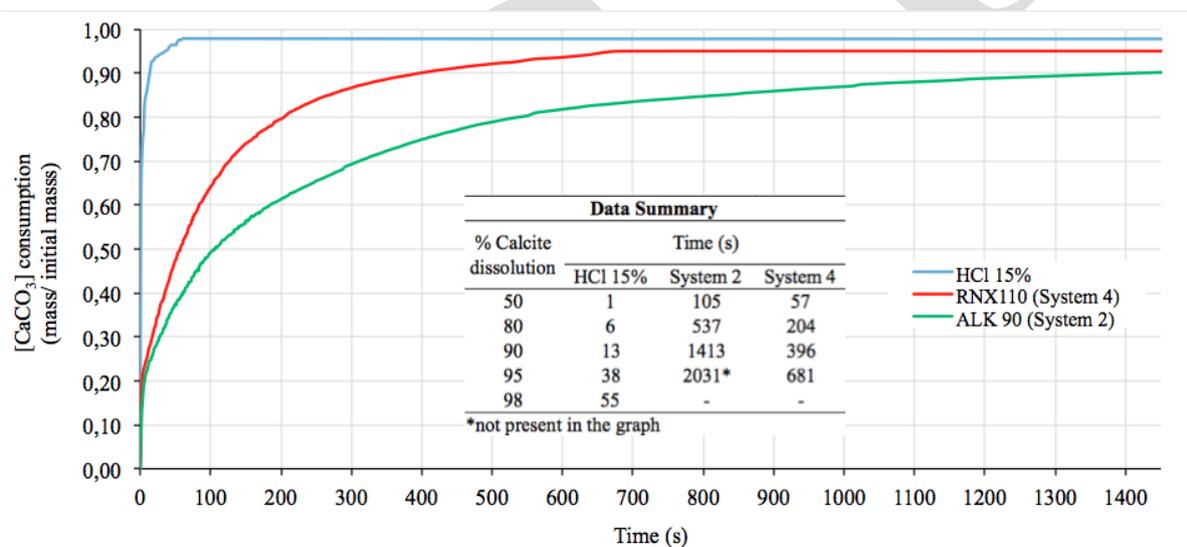


Fig 7: CaCO_3 consumption in microemulsified acid media and in HCl 15% solution

To determine the rheological modification caused by the reaction of the acid systems with the calcium carbonate, rheological measurements of the systems 2 and 4 were made before and after the reaction. Rheological parameters are important in pump operations to determine the energy necessary to perform the operation. In addition, the divergence during flow into pore space depends of fluid rheology [17].

Table 4 shows the results of the rheological parameters for the microemulsion systems before and after the dissolution reaction. Initially, system 2 presented a pseudoplastic behavior ($n < 1$) and the system 4 showed a Newtonian behavior ($n \approx 1$). Both systems after the reaction with the calcium carbonate exhibit a pseudoplastic behavior ($n < 1$) and show an increase in the rheological parameters. System 2, the most efficient in retarding the reaction, showed a higher value of viscosity after the acid reaction. This behavior contributed to the

reduction of the reaction rate observed in themicroemulsifiedmedia,offering more resistance in the acid diffusion process.

Table 4. Values of the rheological parametersfor Ostwald-de-Waele model, before and after (AR) the dissolution reaction

Parameters (Ostwald-de-Waele model)	Systems			
	2	2(AR)	4	4(AR)
Consistency index, $K (Pa.s^n)$	0,0732	0,6700	0,0473	0,1388
Behavior index, $n (Pa.s)$	0,9079	0,7091	0,9924	0,9059
Dynamic viscosity, $\mu_{ap}(cP) \text{ at } 400 \text{ s}^{-1}$	0,0464	0,1173	0,0453	0,0790
R^2	0,9943	0,9929	0,9994	0,9919

Coreflood experiments

Coreflood injection experiments were performed with the microemulsifiedacidsystems 2, 4, and with HCl 15% solution. The main objective was to evaluate the increase of the permeability and the wormhole formation in the cores. Table 5 shows the results forinitial rock permeability(K_i)and after the acid injection(K_a). ΔK and $K_{increment}$ represent the variationand the increment in the corepermeability, respectively.

Table 5. Results of the acid systems injectioninto carbonate cores

System	Porosity	K_i (mD)	K_a (mD)	ΔK (mD)	$K_{increment}$ (%)	Flow rate (mL/min)
HCl 15%	0,429	118.1	259.8	141.7	120%	0,68
System 2	0,392	189.4	297.9	108.5	57%	0,68
System 4	0,444	232.4	368.7	136.3	59%	0,69

The results showed that the microemulsifiedacid successfully increased the permeability of the cores. The increment in the permeability was 57% for system 2 and 59% for system 4. The HCl 15% solution achieved 120% of permeability increment. Permeability gain indicates that the core was stimulated.Nevertheless, it is important understand the dissolution pattern and check the wormhole formation. Despite the treatment with HCl 15% having showed the highest increase in the permeability, by evaluating the core in Figure 8 one can observe that the face dissolution of the rock, due to the HCl, is consumed in the beginning of the core.

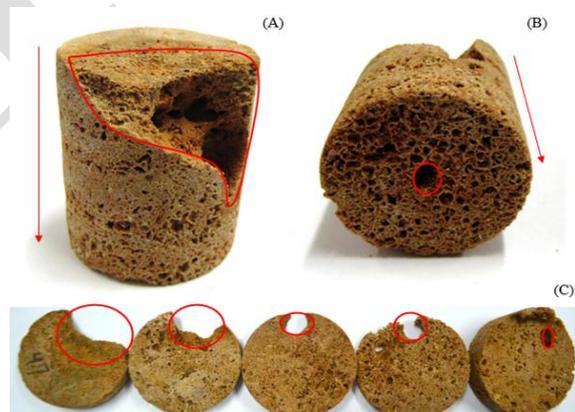


Fig 8: Core after treatment with HCl 15% solution: (a) vertical view; (b) out core face; (c) sectional cuts

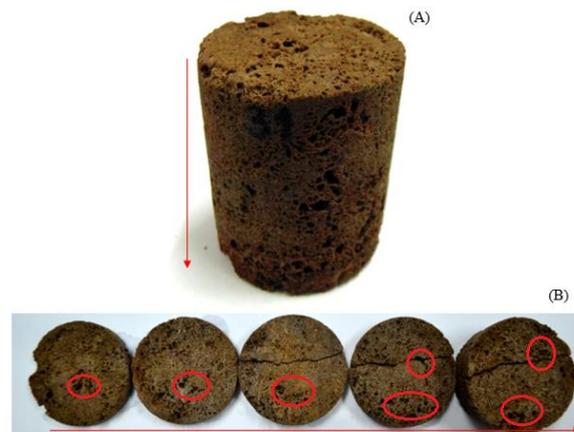


Fig9: Core after treatment with system 2: (a) vertical view; (b) sectional cuts

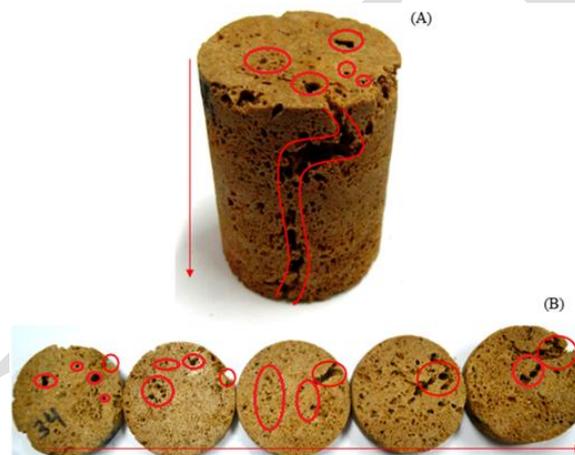


Fig 10: Core after treatment with system 4: (a) vertical view; (b) sectional cuts

Figures 9 and 10 show the core treated with systems 2 and 4, respectively. One can observe that, for both systems, the rock dissolution pattern was more evenly distributed than the core treated with HCl 15% solution. The channels in these systems show a regular diameter along the core. The two microemulsion systems studied showed better performance than the regular HCl solution, with a slightly better performance to the system 4 that achieve 59% of permeability increasing compared at 57% of permeability increasing for the plug stimulated with the system 2. This small difference is due to the effects related to the difference of initial cores permeability, rheology behavior of the systems after the reaction with the calcium carbonate and the retarded reaction capacity.

CONCLUSION

In this work, were applied two different non-ionic surfactants to obtain new acid O/W microemulsion for application in retarded acid systems. Both surfactants enable the formation of acid microemulsions of the type O/W. The results showed that the acid microemulsions systems obtained were effective to retard the acid dissolution reaction. The time was retarded in 53 times for ALK90 and 18 times for the RNX110 when compared with the dissolution in regular HCl 15%. In add the experiments shows that the microemulsion acid systems were less corrosive than regular HCl aqueous solution. Core flood experiments confirmed the

ability of the acid microemulsified systems to increase the rock permeability and promote wormhole formation. The performance of both systems studied was very similar, increasing the permeability near 60%. Even higher the permeability increase provided by the HCl 15%, face dissolution was observed. For the acid microemulsions systems the dissolution pattern was more distributed and no face dissolution was observed. Therefore, the systems obtained have a good potential to be applied as retarded acid systems and may be an alternative to carbonate acidizing fluids.

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