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Crude Oil Foams: Testing and Ranking of Antifoams with the Depressurization Test

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ABSTRACT: The addition of chemicals is the most widely applied solution to prevent the formation of foam or to destroy it immediately after its generation as a result of its simplicity and efficiency. Among the different chemicals that can be used as antifoams or defoamers, polydimethylsiloxane (PDMS) oils are the most common, followed by fluorosilicone oils for the most severe cases. Nonetheless, there is no clear management on the selection of these additives; therefore, it is still based on a trial-and-error basis. For this reason, we have studied the properties and effectiveness of different chemical additives by defining two parameters based on the logistic model developed for the study of the defoaming kinetics of crude oil foams formed by depressurization: the effect on the foamability or antifoamability effect (AE) and the effect on foam stability or destabilization effect (DE). Finally, we have tried to go further in the understanding of the mechanisms involved in foam breaking, looking for similitudes on the defoaming behavior in the different crude oils tested.

INTRODUCTION

Dealing with unwanted foams during crude oil exploitation is a major issue. Big efforts have been carried out to prevent or destroy foams formed in the gas–liquid separator because the presence of foam reduces the production capacity. Furthermore, the presence of foam may damage the separation unit and the equipment downstream, leading to a shutting down of the refining process, causing a big economic loss.^{1–5}

Several techniques have been developed to prevent foam formation or to improve its breaking up, such as spraying water onto the surface, mechanical breaking, increasing of the operational temperature, removal of the foamy agents, or using specially designed units.^{2,4} However, the most common method for foam control is still the addition of chemicals because of its ease of use as well as its effectiveness.^{5–11} In this case, special chemical agents are added to prevent foam formation (antifoamers) or to destroy the foam already created (defoamers).

Industrial experience from the oil industry has shown that, among the different molecules that can be used as antifoaming or defoaming agents, silicone oils are the most effective molecules. Actually, polydimethylsiloxane (PDMS) oils are the most common antifoam agents used in the oil industry, followed by fluorosilicone oils for the most severe cases.^{7,12–14} Actually, some recent works are focused on the evaluation of these chemicals as antifoams in crude oil samples.^{15–17}

Nevertheless, there are other kinds of molecules that can be used as antifoams, principally phosphate esters, metallic soaps of fatty acids, sulfonate compounds, amides, polyglycols, glycol ethers, and alcohols. These molecules usually exhibit less antifoaming effect than silicone oils, but they biodegrade faster than PDMS. In addition, their impact on the refining crude oil catalytic processes is negligible, contrary to silicone and silica, which are usually catalytic poisons. For instance, several non-silicone agents have been tested in a heavy crude oil from north

Alberta (diluted with 10% heptane), showing that a sulfosuccinate of sodium and a dispersion of long-chain fatty alcohols in water have a significant antifoaming effect.¹¹

Despite the efforts carried out to understand the non-aqueous foam breaking mechanism, the selection of industrial antifoaming agents is still based on a trial-and-error basis, with no clear management. There are other considerations to take into account apart from the chemical structure of the surfactant: the solubility of the antifoaming agent, the presence of solids or gels on the gas–liquid interface, the oil and gas composition and properties, the operating conditions (thermal stability of the agent), or the impact that the agent may have in the post-treatment of crude oil.

It is noteworthy that most of the literature on defoaming and antifoaming chemicals is focused on the breaking of aqueous foams. Therefore, the theoretical developments concerning the mechanisms of defoaming were mainly performed on these systems.¹⁸

Two different mechanisms have been proposed for aqueous foam breaking by non-soluble oils: fluid entrainment or pinch-off.^{5,6} In the first mechanism, an antifoam droplet spreads onto the gas–liquid surface, entraining the subjacent fluid with it and, by this way, creating a local film thinning and rupture. On the other hand, in the second mechanism, an antifoam droplet bridges the interface, creating a capillary instability, which destroys the liquid film. In both cases, the first condition needed is the entering of the antifoam droplet into the film lamellae. The definitions of the entering coefficient ($E_{a/i}$), the spreading coefficient ($S_{a/i}$), and the bridging coefficient ($B_{a/i}$) have been made based on thermodynamic criteria for capillary

stability of the foam lamellae as a function of the different surface energies in the system

$$E_{a/i} = \sigma_{w/g} + \sigma_{w/a} - \sigma_{a/g} \quad (1)$$

$$S_{a/i} = \sigma_{w/g} - \sigma_{w/a} - \sigma_{a/g} \quad (2)$$

$$B_{a/i} = \sigma_{w/g}^2 + \sigma_{w/a}^2 - \sigma_{a/g}^2 \quad (3)$$

where σ is the surface tension and the subscripts w, g, and a refer to water, gas, and antifoam, respectively. On the other hand, Denkov differentiates between two types of antifoams: “fast” and “slow”.¹⁹ The main property that differentiates between both types is the barrier to drop entry. This entry barrier has been defined as a function of the critical capillary pressure or the disjoining pressure,^{6,19–21} where the threshold value of the entry barrier is somewhere between 15 and 20 Pa, which separates the fast antifoam region from the slow antifoam region. These mechanisms have been developed for three immiscible phases, i.e., water, gas, and an oily phase containing the antifoam. However, having positive values of these coefficients does not guarantee foam destruction, but they provide a basis for using these types of antifoams. With regard to crude oil foams, other considerations must be taken into account. First of all, the antifoam is usually injected, dissolved, or dispersed in an organic phase instead of an aqueous phase; therefore, it is hard to predict the aggregation state of the antifoams and, thus, the validity of these mechanisms. Furthermore, the solubility of the antifoaming agent, the presence of solids or gels on the gas/liquid interface, or the effect of the additive on downstream processes are also important to the selection of the additive. However, some authors have hypothesized that antifoams should work by spreading onto the gas–liquid interface.¹¹

As highlighted previously, the selection of additives and the prediction of foam behavior after chemical addition are quite complex and no mechanism has yet been clearly established for its understanding. The scope of this work was to develop a methodology for the study and ranking of chemical additives. This methodology is mainly based on the depressurization foaming test that has been presented and thoroughly described in a previous paper.²² Furthermore, we propose a new way to study and compare the effect of the antifoaming chemical additives in terms of impact on both foamability and foam stability.

MATERIALS AND METHODS

Fluid Selection. Four crude oils with different American Petroleum Institute (API) gravities have been chosen to perform antifoaming tests. Their properties are summarized in Table 1. In all cases, crude oils were dehydrated (<0.5% H₂O). A rheological characterization was performed using a rheometer with imposed stress (Haake RS150). In this work, we have used coaxial cylinders (stator-type Z40 smooth with an inner diameter of 43.4 mm and rotor-type

Table 1. Crude Oil Properties: Density (ρ), API Gravity, Viscosity (μ), and Surface Tension (σ)

crude oil	ρ at 20 °C (kg/m ³)	API gravity (deg)	μ at 20 °C (mPa s)	σ at 20 °C (mN/m)
Z1	890	27	37	25.4
Z2	908	24	76	27.5
M1	921	22	173	27.8
M2	921	22	185	28.9

Z40 smooth with an inner diameter of 40 mm diameter) with shear rates between 0 and 1000 s⁻¹ at different temperatures (from 20 to 40 °C). The density was measured with a densimeter Anton Paar DMA 4500M between 20 and 60 °C. The checking of the water content was made using a Metrohm 787 Titrino, which measures the amount of water by the Karl Fischer method. The surface tension was obtained using a drop tensiometer Krüss DSA 25 at a laboratory temperature (20 ± 2 °C).

Several silicone oils have been used as antifoam agents: four different PDMS silicones with different kinematic viscosities, two modified PDMS silicones, three hydroxyl-terminated PDMS, and two fluorosilicones. The antifoam solutions were created by diluting the selected silicone in an adequate solvent at 30% in volume. The properties of the different silicones and the solvent used are gathered in Table 2.

Crude Oil Foam Tests. The depressurization foaming test that we have developed in our laboratory has been thoroughly described in a recent paper.²² This test is similar to the test developed by Fraga et al.,^{15–17} but with some modifications in the design of the test, as in the data treatment and analysis. The principle is shown in Figure 1. The system consists of a high-pressure–high-temperature (HP–HT) aging cell made of stainless steel. After saturation of the crude oil with gas at a fixed pressure under agitation, the cell is depressurized by the instant opening of the ball valve. The mixture of oil and gas flows through a needle valve and a coil tube and fills a graduated glass tube. When the foam volume reaches the desired level (50 mL in our tests), the ball valve is immediately closed and the evolutions of both the air/foam and foam/liquid interfaces are recorded with a camera. The presence of the needle valve is the major difference between this test setup and the setup by Fraga et al. The purpose of this valve is to create a sufficient pressure drop, allowing for the increase of the test repeatability because the system is less impacted by any uncertainty caused by friction differences during the closing of the ball valve. The registered data (total volume V_t and liquid volume V_l) are then processed by means of an image analysis software. In the case of antifoaming tests, the chemical additives to be tested are first diluted in a suitable solvent before being added in the crude oil by means of a precision syringe.

Prior to oil saturation, a desired quantity of antifoam solution is added to the crude oil and the mixture is then agitated (60 min) to homogenize it. All antifoam tests were carried out with 5 bar of saturation gas (CO₂ or CH₄) at a laboratory temperature (20 ± 2 °C). All tests were performed with 40 ppm of surfactant active matter, which is usually recommended by the providers to avoid an overdosing. In all cases, blank tests were performed to determine the effects of the solvent on the foamability and foam stability, showing that both cyclohexane and xylene have no measurable effect, while methyl isobutyl ketone has a slight effect on the foamability but no effect on the stability of the foam.

In the case of crude oils alone, the defoaming kinetic curves exhibit a sigmoidal shape that can be adequately fitted by the logistic model, as presented in a previous paper.²² This model has also been used in the case of foaming tests with chemical additives.²³ The evolution of the normalized volume of foam with time can be described by eq 4, with three adjustable parameters (A_2 , t_0 , and p). In that case, the foam volume is normalized with the maximum quantity of foam that the system can create at the test conditions (V_f/V_f^0) and varies from 100 to 0%. However, it is noteworthy that the volume of foam can also be normalized with respect to the total volume of liquid used in the experiment (V_1^{inf} , i.e., the volume of liquid recovered when all of the foam has broken), as shown by eq 5. Here, the normalized foam volume varies from A'_1 ($V_f^0/V_1^{\text{inf}} > 100\%$) to 0%. This parameter A'_1 , which represents the ratio between the maximum foam volume that is possible to create in the test conditions and the total volume of liquid in the system ($A'_1 = V_f^0/V_1^{\text{inf}}$), can be considered as a foamability index. On the other hand, parameter A'_2 results from the multiplication of A_2 by A'_1 .

Table 2. Silicone Properties (Provided by the Supplier) and Solvent Used for the Antifoaming Solution^a

silicone	type	ρ (kg/m ³)	ν (cSt)	provider	solvent
S1	PDMS	970	1000	Bluestar Silicones	cyclohexane
S2	PDMS	970	12500	Bluestar Silicones	cyclohexane
S3	PDMS	973	60000	Bluestar Silicones	cyclohexane
S4	PDMS	973	500000	Bluestar Silicones	cyclohexane
S5	modified PDMS			Bluestar Silicones	cyclohexane
S9	modified PDMS	910	160	Momentive	xylene
SOH1	hydroxylated PDMS	973	14000	Bluestar Silicones	xylene
SOH2	hydroxylated PDMS	973	50000	Bluestar Silicones	xylene
SOH3	hydroxylated PDMS	973	135000	Bluestar Silicones	xylene
FS1	fluorosilicone	1120	20000	Momentive	cyclohexane
FS2	fluorosilicone	1248	10000	Dow Corning	MIBK

^aMIBK = methyl isobutyl ketone.

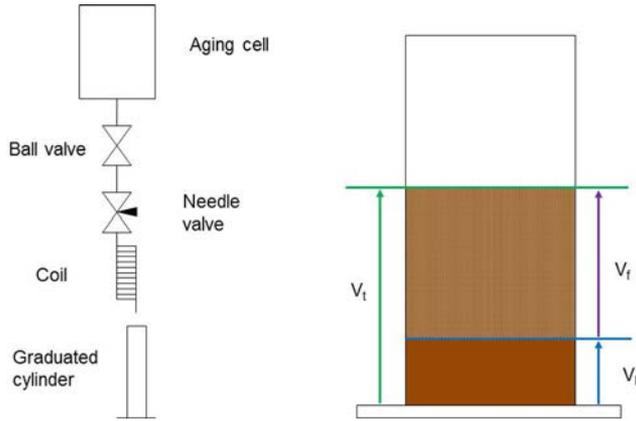


Figure 1. Principle of the foaming test by depressurization (left) and parameters recorded during the foaming test in the graduated test tube (right).

$$\frac{V_f}{V_f^0} = \frac{1 - A_2}{1 + \left(\frac{t}{t_0}\right)^p} + A_2 \quad (4)$$

$$\frac{V_f}{V_l^{inf}} = \frac{A'_1 - A'_2}{1 + \left(\frac{t}{t_0}\right)^p} + A'_2 \quad (5)$$

Antifoamability Effect and Destabilizing Effect Definitions.

We have defined two criteria based on eqs 4 and 5 parameters to simplify the comparison between the different chemical additives in terms of effect on the foamability (i.e., the effect on the initial foam volume) and foam stability (i.e., the effect on the foam volume after a certain period of time).

The antifoamability effect (AE) can be defined as the capacity of a surfactant to prevent foam formation or to reduce the amount of foam created. In our case, we have related this property to the foamability index, defined as the maximum amount of foam that the system can create at the test conditions. Mathematically, it can be expressed as shown in eq 6.

$$AE = \frac{A'_{1,with\ antifoam} - A'_{1,without\ antifoam}}{A'_{1,without\ antifoam}} \times 100 \quad (6)$$

This new index is expressed as a percentage and shows the reduction rate of the foam created compared to the oil system without additive. Therefore, antifoamers can be easily classified according to their effectiveness. If $AE > 0$, then the chemical shows a foaming effect. If $AE = 0$, then the chemical has no effect. If $AE < 0$, then the chemical prevents foam formation, with the effect being all the more important as the absolute value of AE is high.

The destabilizing effect (DE) is defined as the effect of the chemical compound on the foam stability. It can be related to the end-life time of the foam but it is worth noting that the different additives may have a different impact on the different stages of the life of the foam. To take this into account, we have defined the effect on the foam stability

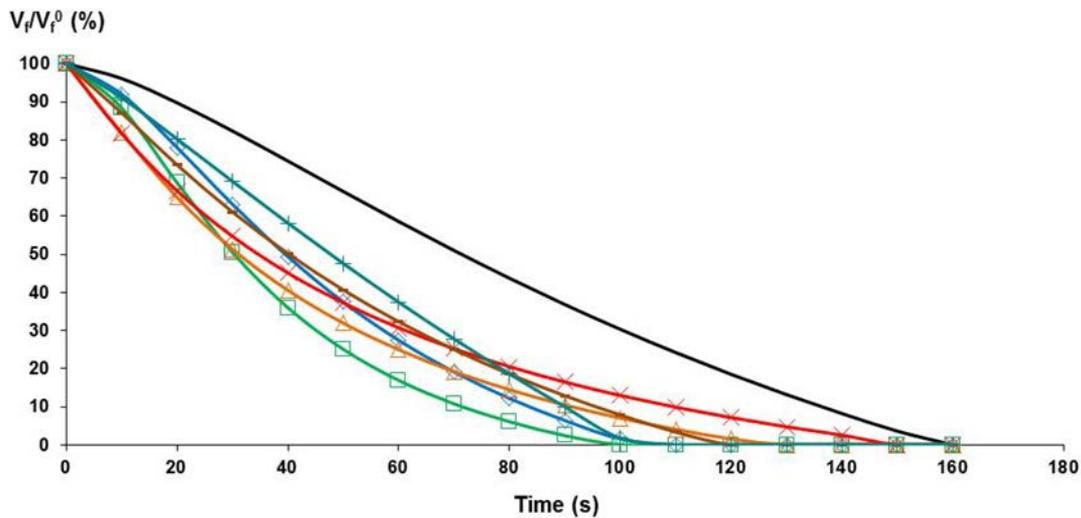


Figure 2. Modeled defoaming kinetic of crude oil Z1 (black line) with respect to chemical additive defoaming kinetics with 5 bar of CO₂: S1 (empty blue diamonds), S2 (empty green squares), S3 (empty orange triangles), S4 (red crosses), FS1 (brown dashes), and FS2 (greenish plus signs).

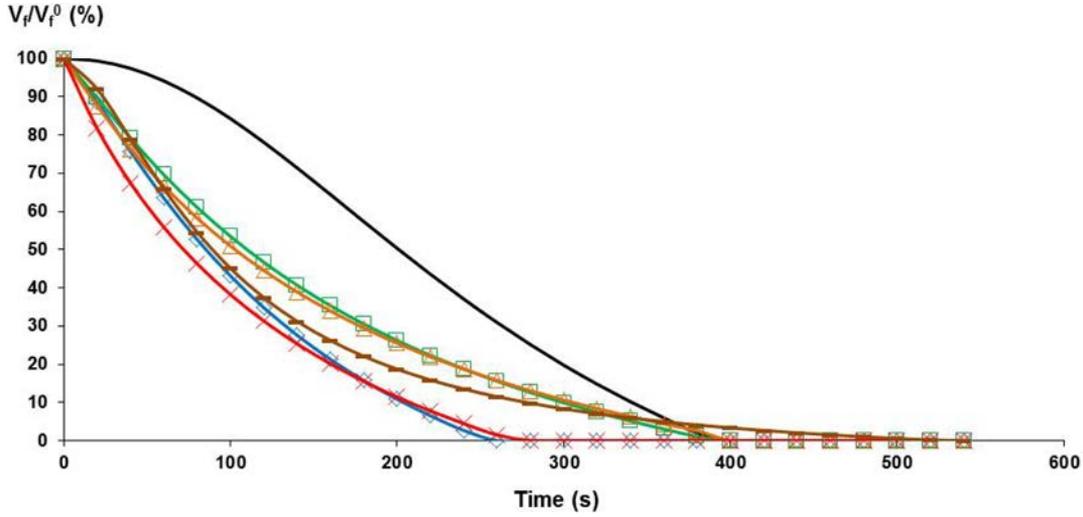


Figure 3. Modeled defoaming kinetic of crude oil M1 (black line) with respect to chemical additive defoaming kinetics with 5 bar of CO₂: S1 (empty blue diamonds), S2 (empty green squares), S3 (empty orange triangles), S4 (red crosses), and FS1 (brown dashes).

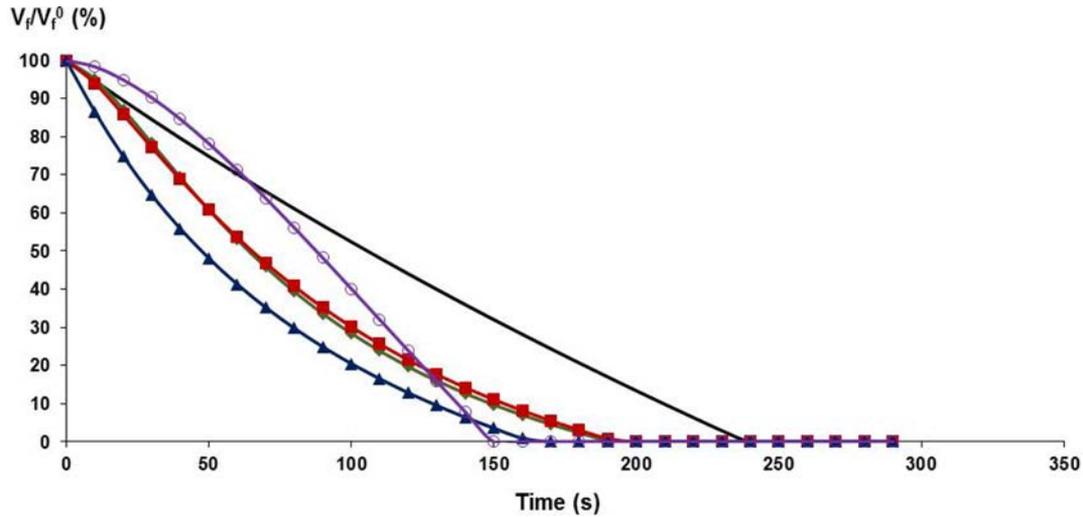


Figure 4. Modeled defoaming kinetic of crude oil Z2 (black line) with respect to chemical additive defoaming kinetics with 5 bar of CO₂: SOH1 (dark green diamonds), SOH2 (dark red squares), SOH3 (dark blue triangles), and S9 (empty purple circles).

as a function of two indexes, which compare both half-life ($t_{50\%}$) and end-life (t_f) times of foams with and without antifoam. It is noteworthy not to confuse this effect with a defoamer effect because a defoamer is added once the foam is already created, while in our tests, the additive is mixed with the crude oil prior to foam tests. These two indexes can be expressed as follows:

$$DE I = \frac{t_{50\%, \text{with antifoam}}}{t_{50\%, \text{without antifoam}}} \quad (7)$$

$$DE II = \frac{t_{f, \text{with antifoam}}}{t_{f, \text{without antifoam}}} \quad (8)$$

Therefore, as in the case of AE, surfactants can be classified according to their destabilizing effect. If DE I < 1 and DE II < 1, then the chemical shows a significant destabilizing effect. If DE I < 1 and DE II > 1, then the chemical acts at early stages of the lifetime of the foam with a stabilizing effect at the end of its life. If DE I > 1 and DE II < 1, then the chemical stabilizes the foam at the early stages of the lifetime of the foam but has a destabilizing effect at the end. If DE I > 1 and DE II > 1, the chemical stabilizes the foam.

RESULTS AND DISCUSSION

Additive Efficiency in Crude Oils with CO₂. All tests were carried out in the same conditions, i.e., with 5 bar of CO₂ at controlled room temperature (20 ± 2 °C) and with 40 ppm of active matter of silicone additive. Each test was performed at least 3 times, with a maximum deviation of 10% for the foam volume and 7% for total and free liquid volumes. In addition, for modeling, at least three valid tests have to be considered. However, as a result of oil sample availability, we were not able to test all silicone additives with the same oil. The different tests performed are described as follows: oil Z1, silicones S1, S2, S3, and S4 and fluorosilicones FS1 and FS2; oil M1, silicones S1, S2, S3, and S4 and fluorosilicone FS1; oil Z2, silicones SOH1, SOH2, and SOH3 and modified silicone S9; and oil M2, silicones SOH1, SOH2, and SOH3, modified silicones S5 and S9, and silicone S2.

Figures 2–5 show the best fitted curve given by eq 4 for each oil. The parameters of the model are displayed in Tables 3 and 4. With regard to these figures, it is possible to observe that each additive has a different effect on the behavior of the foam.

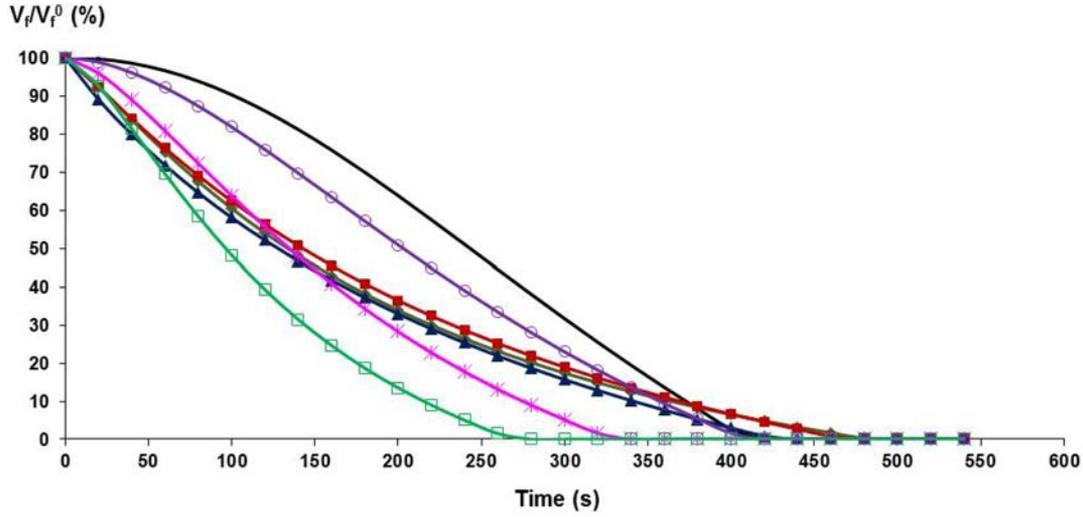


Figure 5. Modeled defoaming kinetic of crude oil M2 (black line) with respect to chemical additive defoaming kinetics with 5 bar of CO₂: SOH1 (dark green diamonds), SOH2 (dark red squares), SOH3 (dark blue triangles) S2 (empty green squares), S5 (pink asterisks), and S9 (empty purple circles).

Table 3. Logistic Model Parameters (eqs 4 and 5) for Oil Samples Z1 and Z2 with 40 ppm of Silicone Additive and 5 bar of CO₂^a

oil sample	silicone	gas	eq 4					eq 5			
			A_2	t_0	p	R^2	χ^2	A'_1	A'_2	R^2	χ^2
Z1		CO ₂	-85 ± 12	142 ± 11	1.45 ± 0.15	0.967	31	179 ± 10	-152 ± 16	0.941	192
		S1	-36 ± 7	55 ± 9	1.62 ± 0.21	0.965	31	150 ± 11	-53 ± 9	0.959	112
		S2	-18 ± 6	36 ± 3	1.72 ± 0.14	0.981	18	139 ± 6	-25 ± 4	0.984	39
		S3	-30 ± 4	46 ± 7	1.19 ± 0.12	0.964	25	145 ± 9	-44 ± 6	0.958	91
		S4	-35 ± 4	57 ± 12	1.06 ± 0.11	0.961	24	153 ± 9	-54 ± 6	0.963	77
		FS1	-64 ± 8	81 ± 7	1.17 ± 0.15	0.984	11	158 ± 11	-101 ± 12	0.975	61
		FS2	-204 ± 127	186 ± 79	1.20 ± 0.15	0.982	16	192 ± 21	-388 ± 79	0.887	302
Z2		CO ₂	-432 ± 13	1055 ± 57	0.99 ± 0.07	0.992	7	221 ± 7	-950 ± 36	0.986	65
		SOH1	-32 ± 10	90 ± 11	1.49 ± 0.13	0.966	29	173 ± 8	-55 ± 6	0.966	98
		SOH2	-43 ± 8	104 ± 10	1.34 ± 0.07	0.989	9	175 ± 4	-75 ± 4	0.988	32
		SOH3	-65 ± 6	107 ± 7	1.02 ± 0.10	0.972	19	180 ± 6	-116 ± 7	0.976	71
		S9	-245 ± 48	259 ± 28	1.64 ± 0.17	0.964	35	222 ± 8	-534 ± 27	0.962	208

^a R^2 and χ^2 are statistical parameters.

Table 4. Logistic Model Parameters (eqs 4 and 5) for Oil Samples M1 and M2 with 40 ppm of Silicone Additive and 5 bar of Gas^a

oil sample	silicone	gas	eq 4					eq 5			
			A_2	t_0	p	R^2	χ^2	A'_1	A'_2	R^2	χ^2
M1		CO ₂	-50 ± 5	281 ± 9	2.08 ± 0.14	0.980	24	277 ± 9	-137 ± 11	0.968	304
		S1	-51 ± 7	150 ± 12	1.25 ± 0.17	0.935	42	168 ± 9	-86 ± 8	0.962	105
		S2	-45 ± 7	194 ± 18	1.13 ± 0.05	0.985	9	162 ± 4	-73 ± 3	0.982	38
		S3	-42 ± 18	183 ± 46	1.06 ± 0.12	0.904	63	163 ± 9	-68 ± 7	0.920	185
		S4	-59 ± 15	158 ± 32	0.99 ± 0.08	0.985	7	156 ± 5	-92 ± 5	0.988	25
		FS1	-7 ± 2	96 ± 3	1.60 ± 0.08	0.974	12	146 ± 4	-10 ± 2	0.982	28
M2		CO ₂	-97 ± 10	405 ± 19	2.12 ± 0.33	0.949	48	302 ± 23	-272 ± 19	0.968	338
		SOH1	-37 ± 16	212 ± 44	1.20 ± 0.13	0.950	38	180 ± 14	-67 ± 11	0.894	270
		SOH2	-57 ± 9	282 ± 17	1.11 ± 0.09	0.976	18	195 ± 8	-111 ± 8	0.969	86
		SOH3	-84 ± 7	359 ± 25	0.96 ± 0.07	0.976	16	184 ± 7	-154 ± 9	0.966	78
		S9	-69 ± 8	332 ± 17	1.76 ± 0.17	0.957	37	300 ± 14	-203 ± 17	0.952	369
		S2	-40 ± 19	144 ± 29	1.46 ± 0.21	0.949	26	179 ± 14	-72 ± 9	0.955	71
		S5	-54 ± 17	219 ± 33	1.50 ± 0.13	0.981	15	202 ± 12	-108 ± 11	0.965	107
		CH ₄	-106 ± 8	550 ± 23	1.45 ± 0.08	0.984	14	231 ± 6	-243 ± 9	0.984	75
		S2	-17 ± 3	169 ± 6	1.71 ± 0.06	0.993	5	175 ± 4	-30 ± 2	0.994	13

^a R^2 and χ^2 are statistical parameters.

Table 5. Effects on Foamability (AE) and Foam Stability (DE) of Silicones on Different Crude Oils with 5 bar of CO₂ and 40 ppm of Active Matter^a

oil	additive	AE (%)	AE?	DE I	DE II	DE?
Z1	S1	-16	✓	0.55 ± 0.06	0.66 ± 0.10	✓✓
	S2	-22	✓	0.42 ± 0.03	0.62 ± 0.09	✓✓
	S3	-19	✓	0.44 ± 0.04	0.80 ± 0.16	✓✓
	S4	-14	✓	0.49 ± 0.06	0.97 ± 0.27	✓×
	FS1	-12	✓	0.56 ± 0.06	0.75 ± 0.11	✓✓
	FS2	7	×	0.67 ± 0.28	0.65 ± 0.29	✓✓
M1	S1	-39 ± 1	✓	0.42 ± 0.02	0.65 ± 0.07	✓✓
	S2	-42 ± 1	✓	0.55 ± 0.04	1.00 ± 0.18	✓×
	S3	-41 ± 1	✓	0.51 ± 0.08	1.05 ± 0.54	✓×
	S4	-44 ± 1	✓	0.36 ± 0.03	0.69 ± 0.14	✓✓
	FS1	-47 ± 1	✓	0.44 ± 0.01	1.35 ± 0.45	✓×
	Z2	SOH1	-22 ± 1	✓	0.61 ± 0.09	0.81 ± 0.19
Z2	SOH2	-21 ± 1	✓	0.62 ± 0.08	0.81 ± 0.14	✓✓
	SOH3	-18 ± 1	✓	0.45 ± 0.04	0.69 ± 0.08	✓✓
	S9	0.7 ± 0.1	×	0.83 ± 0.18	0.63 ± 0.08	✓✓
M2	SOH1	-40 ± 3	✓	0.55 ± 0.08	1.18 ± 0.59	✓×
	SOH2	-35 ± 2	✓	0.59 ± 0.05	1.14 ± 0.24	✓×
	SOH3	-39 ± 2	✓	0.52 ± 0.04	1.04 ± 0.14	✓×
	S2	-41 ± 3	✓	0.40 ± 0.04	0.66 ± 0.17	✓✓
	S5	-33 ± 2	✓	0.55 ± 0.07	0.80 ± 0.17	✓✓
	S9	-0.6 ± 0.1	×	0.83 ± 0.09	1.00 ± 0.11	✓×

^a✓, the additive has an effect; ×, the additive has a very small or no effect. The best additive is in bold.

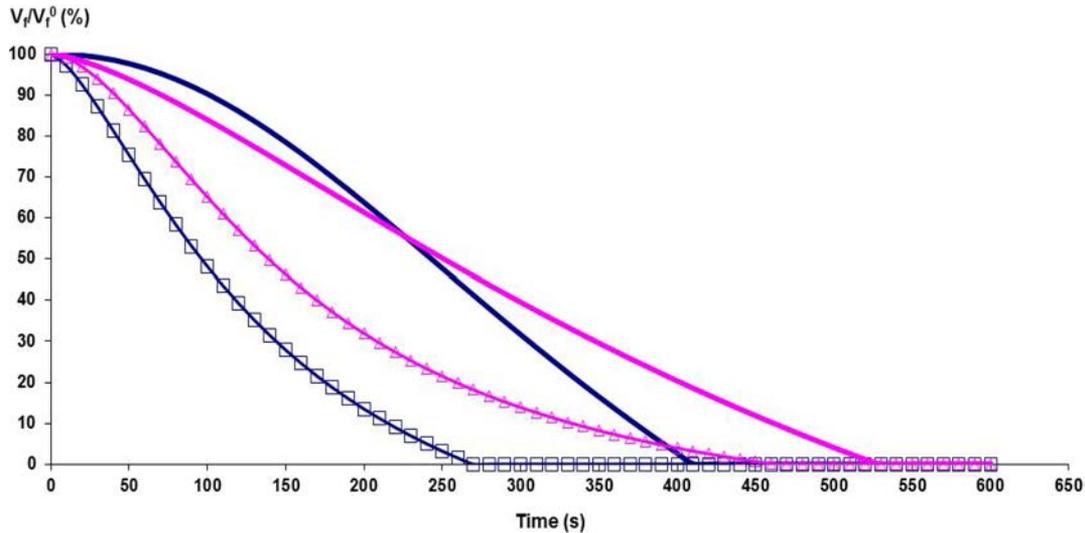


Figure 6. Modeled defoaming kinetic of crude oil M2 without additive with CO₂ (dark blue line) and with CH₄ (pink line) and with 40 ppm of silicone S2 with CO₂ (empty dark blue squares) and with CH₄ (empty pink triangles).

In all cases, it is possible to notice a destabilizing effect, which varies in function of the oil used. There are three principal behaviors: a complete destabilizing effect, where the foam breakdown is faster with the addition of the silicone, an initial destabilizing effect followed by a stabilization effect at the end of the lifetime of the foam (see Figures 2 and 4), and the particular defoaming kinetic of silicone S9, which exhibits a completely different behavior from the other additives (see Figure 4 and 5). This silicone tends to stabilize the foam at the first stages of the lifetime of the foam (even more than crude oil alone for the case of oil Z2; Figure 4), and then the destruction of the foams takes place in a nearly linear manner.

To compare the efficiency of each additive and the effect of the crude oil, we have estimated the values of the destabilizing

effect as shown in eqs 7 and 8 (see Table 5). On the one hand, all additives have a value of DE I lower than 1, which shows that, in all cases, the half-life time of the foam is reduced. As said before, it is worth mentioning the case of silicone S9, for which the DE I values are 0.83 for both oils Z2 and M2. For these oils, this silicone shows less effect than the other silicones at the early stages of the lifetime of the foam. On the other hand, the effectiveness of the silicones varies a lot with regard to the destabilizing effect at the end-life time of the foam (DE II). Some of the additives have a small impact on the foam lifetime (silicone S4 in oil Z1), no effect (silicone S2 in oil M1 or S9 in oil M2), or the opposite effect (silicones SOH1 and SOH2 in oil M2 or FS1 in oil M1). In addition, it is possible to observe that the crude oil also has an impact on the additive efficiency.

For instance, silicone S2 is the most performing in terms of foam breaking in oils Z1 and M2 but not in oil M1 (no effect at the end of the lifetime of the foam). In the same way, fluorosilicone FS1 is quite performing in oil Z1 but increases the lifetime of oil M1 by 35%. This leads to the deduction that the crude oil properties and composition have a strong impact on the additive effectiveness.

With regard to the effect on foamability AE (eq 6 and Table 5), almost all additives exhibit a significant effect. Furthermore, if we compare the results oil by oil, we observe that the effectiveness is of the same order of magnitude for each additive, except S9 and FS2. Silicone S9 shows no effect on foamability and can be considered as a pure foam breaker, while fluorosilicone FS2 has a foaming effect despite the reverse effect of its solvent ($AE_{\text{MIBK}} = -9.5\%$).

When both effects (AE and DE) are taken into account, it is possible to select the most performing additive for each crude oil. For oils Z1 and M2, the most effective silicone is S2. For oil Z2, hydroxylated silicone SOH3 shows the strongest destabilizing effect. For oil M1, silicones S1 or S4 both have similar performances.

Effect of the Saturation Gas. The nature of the saturation gas may have an impact on the behavior of the foam.²² For this reason, we have tested silicone S2 in crude oil M2 using methane as the saturation gas, because it is more representative of the associated gas encountered on the field than CO₂. The effect of the nature of the gas on both defoaming curves with and without additive is displayed in Figure 6. With the effect of the additive, it is possible to observe that silicone has a destabilizing effect with both gases. Moreover, the shape of both curves is similar. However, in both cases (with and without additive), foams with CH₄ are more stable than foams with CO₂ (see Figure 6 and Table 6). Also, it is worth

Table 6. Effects on Foamability (AE) and Foam Stability (DE) of Silicone S2 on Crude Oil M2 with 5 bar of Gas and 40 ppm of Active Matter^a

gas	AE (%)	AE?	DE I	DE II	DE?
CO ₂	-41 ± 3	√	0.40 ± 0.04	0.66 ± 0.17	√√
CH ₄	-24 ± 1	√	0.55 ± 0.02	0.87 ± 0.09	√√

^a√, the additive has an effect; ×, the additive has a very small or no effect.

mentioning that S2 decreases the foamability for both gases, with this effect being stronger for CO₂ than for CH₄. Hence, these results confirm the importance of performing tests on additives using a representative field gas because it has a significant impact on the additive efficiency.

Classical Foam Breaking Mechanisms by Chemical Additives. As mentioned previously, two mechanisms have been proposed to explain foam breaking in aqueous foams by chemical additives: spreading and pinch-off. To check the relevance of these mechanisms in our experiments, we have calculated the entering, the spreading, and the bridging coefficients (eqs 1, 2, and 3, respectively) for crude oil M2 and a silicone additive of each family tested: a PDMS (S2), a modified PDMS (S5), a hydroxylated PDMS (SOH1), and a fluorosilicone (FS1). The surface and interfacial tensions were measured with a drop tensiometer (Krüss DSA 25). The values of each coefficient are displayed in Table 7.

With regard to these values, it is possible to point out that the entering, the spreading, and the bridging coefficients are

Table 7. Entering, Spreading, and Bridging Coefficients of S2, S5, SOH1, and FS1 in M2

additive	$E_{a/o}$ (mN/m)	$S_{a/o}$ (mN/m)	$B_{a/o}$ (mN/m) ²
S2	12.8	5.49	457
SOH1	11.5	7.49	461
FS1	11.2	8.08	465
S5	7.9	0.06	228

very similar for silicones S2, SOH1, and FS1, while the values for silicone S5 are significantly lower. However, silicone S5 is the second most performing additive, even more than SOH1, despite its very low spreading coefficient. It is noteworthy that the lack of correlation between the values of E , S , and B coefficients and the actual antifoam activity has been reported for aqueous foams and explained with the role of the entry barrier.¹⁹ Unfortunately, it is impossible to clarify here the mechanisms involved in the case of crude oil without using complementary direct methods, such as optical observations or model experiments with foam films and/or plateau borders, which were not performed in the framework of this study.

Defoaming Rates. As seen, several factors may affect the defoaming behavior of a crude oil, such as the composition and physicochemical properties of the oil, the gas forming the foam, but also the properties and nature of the antifoam additive. This makes the understanding of the mechanisms involved in defoaming by chemical additives extremely complex. For this reason, we decided to study the defoaming rates of the crude oils with and without additives.

The foam breaking rate or defoaming rate can be defined as the variation of the foam volume with time. Mathematically, it can be obtained by deriving the defoaming kinetic curve (Figure 7).

$$v_d = \frac{d(V_f/V_f^0)}{dt} \quad (9)$$

According to the defoaming rate, we have found three main zones in the lifetime of the foam. These three zones are shown in Figure 7. Zone I: almost no change in the foam volume is observed in this zone. This is mainly due to the superposition of two effects of opposite nature: on the one hand, the creation and growing of foam by bubble nucleation and bubble ripening and, on the other hand, the processes of foam decline and destruction, such as film drainage, gas diffusion through the atmosphere, and coalescence. In this zone, the rate of foam formation is similar to that of foam destruction, resulting in a constant volume of foam. This zone is not necessarily observed in every foam system, but it is possible to find it in highly viscous oils (as M2 or M1), in high gas saturation oils, and in stabilized foams. Zone II: here, the destruction processes become dominant. Therefore, it is possible to observe an increase of the foam destruction rate until a maximum, which corresponds to the inflection point of the sigmoidal curve. Zone III: this is the last zone observed. Once the inflection point is reached, the destruction rate begins to decrease. This can be explained by the deceleration of the drainage rate as the foam becomes drier as well as the decreasing of the Ostwald ripening phenomenon because the bubble sizes are more homogeneous. Moreover, at this point, some film stabilization phenomena may take place (e.g., Gibbs–Marangoni effect, capillary suction, etc.).

Each zone can be defined by a characteristic defoaming rate: the initial defoaming rate ($v_{d,0}$) for the first zone, the maximal

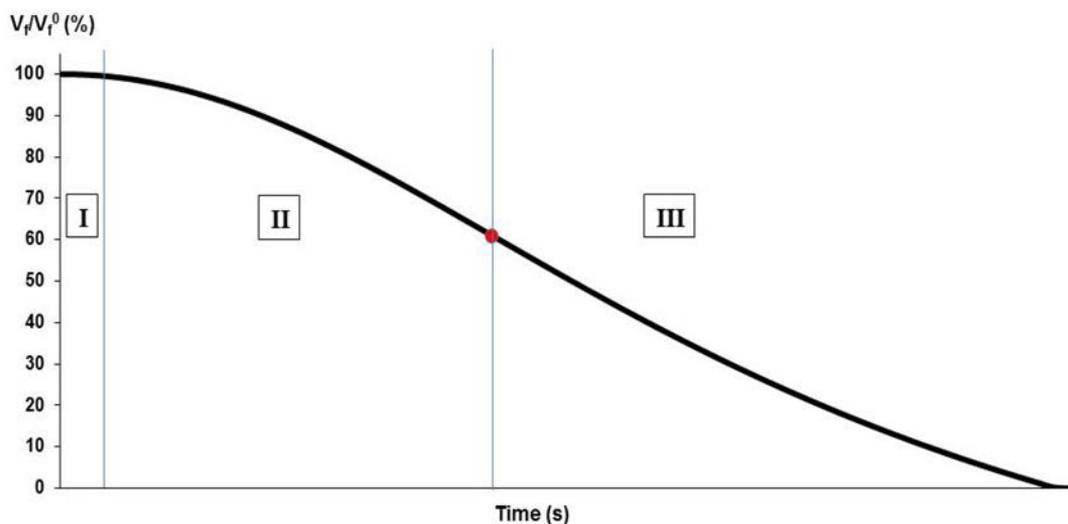


Figure 7. Schematic defoaming curve. The red point represents the inflection point of the curve.

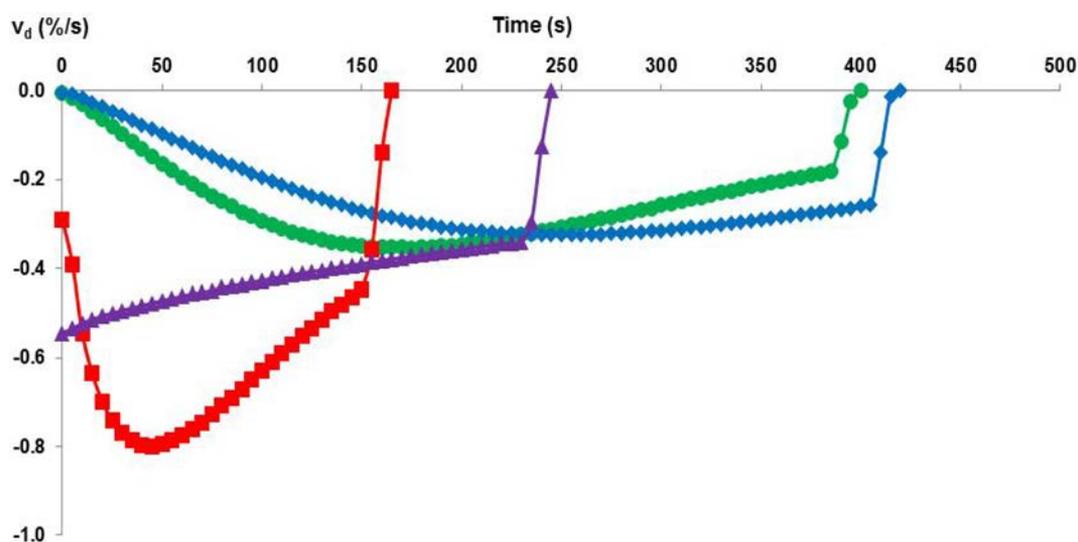


Figure 8. Defoaming rates of crude oils Z1 (red squares), Z2 (purple triangles), M1 (green circles), and M2 (blue diamonds) with 5 bar of CO_2 .

foam breaking rate for the middle zone ($v_{d,\max}$), and the final defoaming rate for the third zone ($v_{d,f}$). We have represented in Figure 8 the defoaming rates of the oils without additive to analyze their different behaviors. Oils M1 and M2 show lower values of defoaming rates because they are more viscous than Z1. Furthermore, these oils have initial values of defoaming rates closer to 0, which corresponds to the presence of the first region described above (see Table 8 and Figures 3 and 5). In addition, oil Z2 exhibits a quasilinear defoaming rate until the end of the lifetime of the foam.

With regard to the impact of the chemical additives, the addition of a few parts per million (ppm) results in an increase

Table 8. Initial, Maximal, and Final Defoaming Rates of Oils Z1, Z2, M1, and M2 with 5 bar of CO_2

crude oil	$v_{d,0}$ (%/s)	$v_{d,\max}$ (%/s)	$v_{d,f}$ (%/s)
Z1	-0.290	-1.468	-0.414
Z2	-0.544	-0.544	-0.217
M1	-0.006	-0.374	-0.089
M2	-0.004	-0.202	-0.081

of the foam breaking rate, as shown in the case of PDMS silicones with oils Z1 and M1 (Figures 9 and 10 and Figures S1 and S2 of the Supporting Information). It is noteworthy that the increase of the defoaming rate is higher in the case of the less viscous oil Z1.

Similar tendencies can be observed in both oils: the initial defoaming rate increases with the viscosity (hence, the size) of the silicone, while the trend reverses once the maximum rate has been reached (rates tend to decrease with increasing viscosity). Actually, an increase of the molecular size leads to the displacement of the maximal defoaming rate through the first stages of the lifetime of the foam, even reaching the initial defoaming rate (as in the case of silicone S4, where the initial defoaming rate corresponds to the maximal defoaming rate). This suggests that PDMS has a strong effect on the second region of the foam kinetics of destruction. The same tendencies have been observed for PDMS-OH (see Figures S3 and S4 of the Supporting Information); therefore, we can think that, in both cases, the additives have a significant effect on the second region of foam breakage kinetics. Finally, we want to point out the special behavior of silicone S9 (Figure S5 of the Supporting

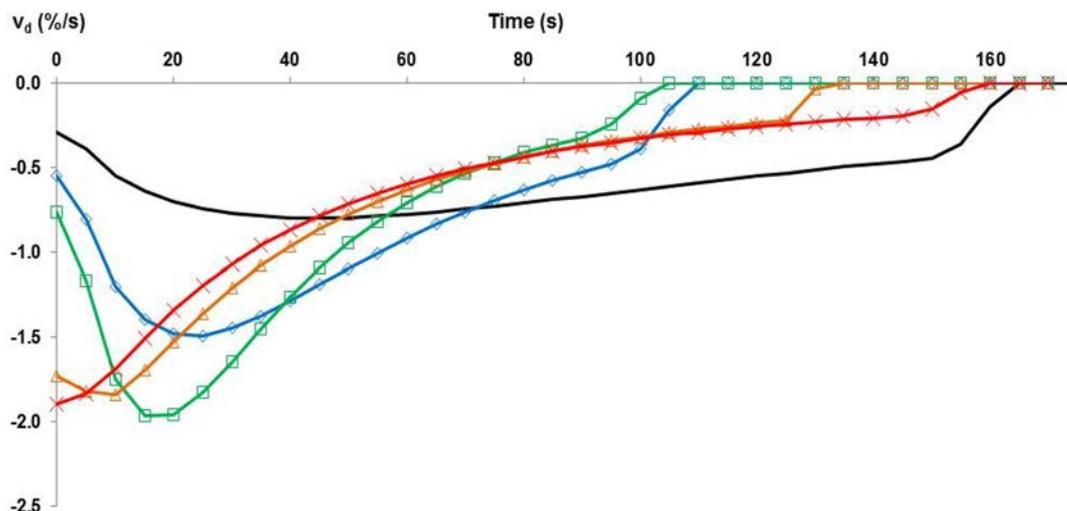


Figure 9. Defoaming rates of crude oil Z1 (black line) with 5 bar of CO₂ and 40 ppm of S1 (empty blue diamonds), S2 (empty green squares), S3 (empty orange triangles), and S4 (red crosses).

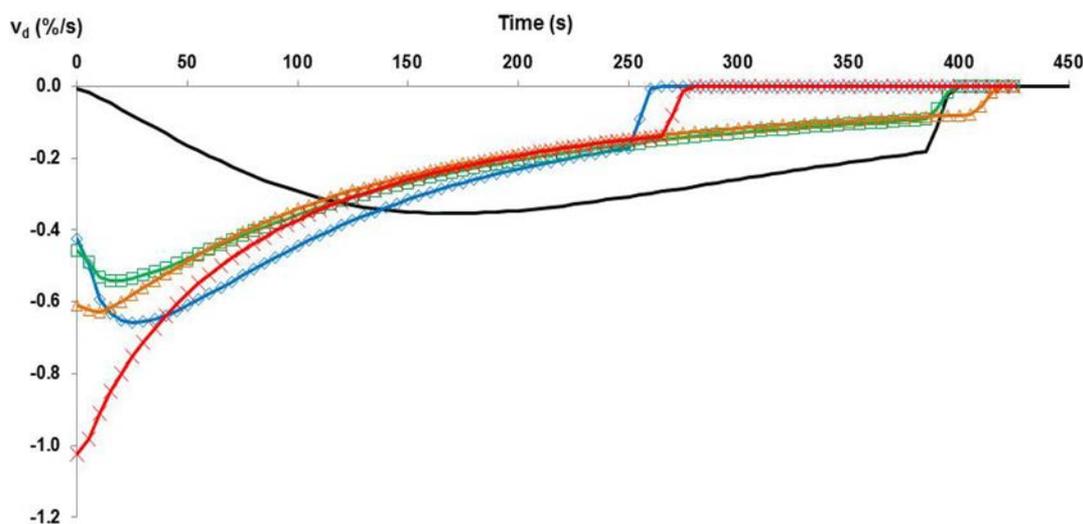


Figure 10. Defoaming rates of crude oil M1 (black line) with 5 bar of CO₂ and 40 ppm of S1 (empty blue diamonds), S2 (empty green squares), S3 (empty orange triangles), and S4 (red crosses).

Information), which shows no effect on the stability or foamability of the initial foam but exhibits a strong destabilizing effect after a while, maintaining high defoaming rates for the whole life of the foam. This leads us to think that this additive acts as a pure destabilizer agent for foam.

CONCLUSION

The addition of chemical additives is the most widely used way to control foaminess in crude oil because of its simplicity and efficiency. Among the different chemicals that can be used, silicone-based antifoams are the most common (essentially PDMS and fluorosilicone). Nevertheless, there are no clear guidelines to select a specific chemical additive for a specific oil; therefore, the selection of the additive is still performed on a trial-and-error basis. For this reason, we have adapted the foaming laboratory test presented in a previous paper to test and rank the effect of different additives on crude oil foam formation by depressurization. To do this, a desired amount of additive is added to the oil prior to gas saturation. The experimental procedure as well as the mathematical models described in the previous part are still valid for this kind of test.

The defoaming kinetic curves were analyzed in terms of foamability reduction (AE) and foam stability reduction (DE) using two parameters based on the logistic model. The definition of these two parameters allows for the selection of the best performing additive for a given crude oil. It is first of all important to keep in mind that the effectiveness of an antifoam additive is not only a function of its chemical properties and nature but also the properties and composition of the crude oil and the nature of the saturation gas. As seen during this study, the best additive selected for one crude oil will not be necessarily adapted to treat another crude oil (as in the case of silicone S2 with oils Z1 and M1). Furthermore, the foaming gas also has a significant impact on the ability of the additive to prevent or destroy foam. For this reason, it is recommended to perform the foaminess tests using a representative field gas.

With regard to the defoaming curves, the behavior of silicones PDMS and PDMS-OH was similar. It was observed that the initial rate of breaking increases with the viscosity (hence, the size) of the silicone. Also, S9 silicone shows a very particular behavior, because it has no impact on the foamability or foam stability at the beginning but, after a while, destroys the

foam at high rates (near its maximum rate) until almost the end of the breaking process.

To conclude, the foaming test by depressurization can be readily used to test and rank different chemical additives, leading to the optimal selection of the chemical in a meaningful and repeatable way. Future objectives will be to identify the relevant parameters that control the mechanism of action of chemicals and to develop consistent approaches to control foaming in complex crude oil systems and to optimize the design of chemicals.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.6b02567.

Normalized defoaming rates of crude oil Z1 (black line) with 5 bar of CO₂ and 40 ppm of S1 (empty blue diamonds), S2 (empty green squares), S3 (empty orange triangles), and S4 (red crosses) (Figure S1), normalized defoaming rates of crude oil M1 (black line) with 5 bar of CO₂ and 40 ppm of S1 (empty blue diamonds), S2 (empty green squares), S3 (empty orange triangles), and S4 (red crosses) (Figure S2), normalized defoaming rates of crude oil Z2 (black line) with 5 bar of CO₂ and 40 ppm of SOH1 (dark green diamonds), SOH2 (dark red squares), and SOH3 (dark blue triangles) (Figure S3), normalized defoaming rates of crude oil M2 (black line) with 5 bar of CO₂ and 40 ppm of SOH1 (dark green diamonds), SOH2 (dark red squares), and SOH3 (dark blue triangles) (Figure S4), and normalized defoaming rates of silicone S9 in crude oil Z2 (empty purple circles) and M2 (purple circles) with 5 bar of CO₂ (Figure S5) (PDF)

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Notes

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