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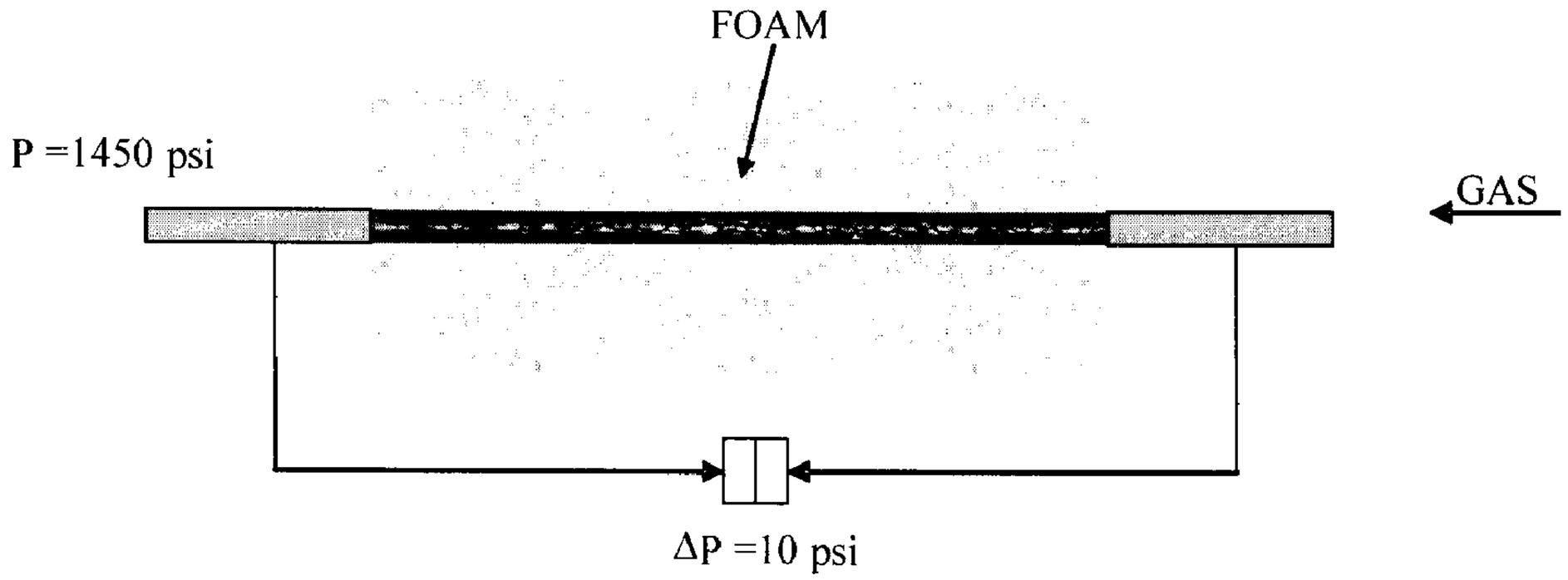
(54) Title: FOAMING COMPOSITION FOR HIGH TEMPERATURE AND SALINITY



(57) Abrégé/Abstract:
The present invention relates to the preparation of foaming formulations for high temperature, salinity and concentration of divalent ions, such as Calcium and Magnesium, that apply the synergistic effect of sodium alpha olefin sulfonates and alkyl amido propyl betaines; said inventions may use, as solvent, water, sea water, connate water, alcohols or mixtures all thereof. Said formulations control the piping of gas in reservoirs of the naturally fractured carbonate type.

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SUMMARY OF THE INVENTION

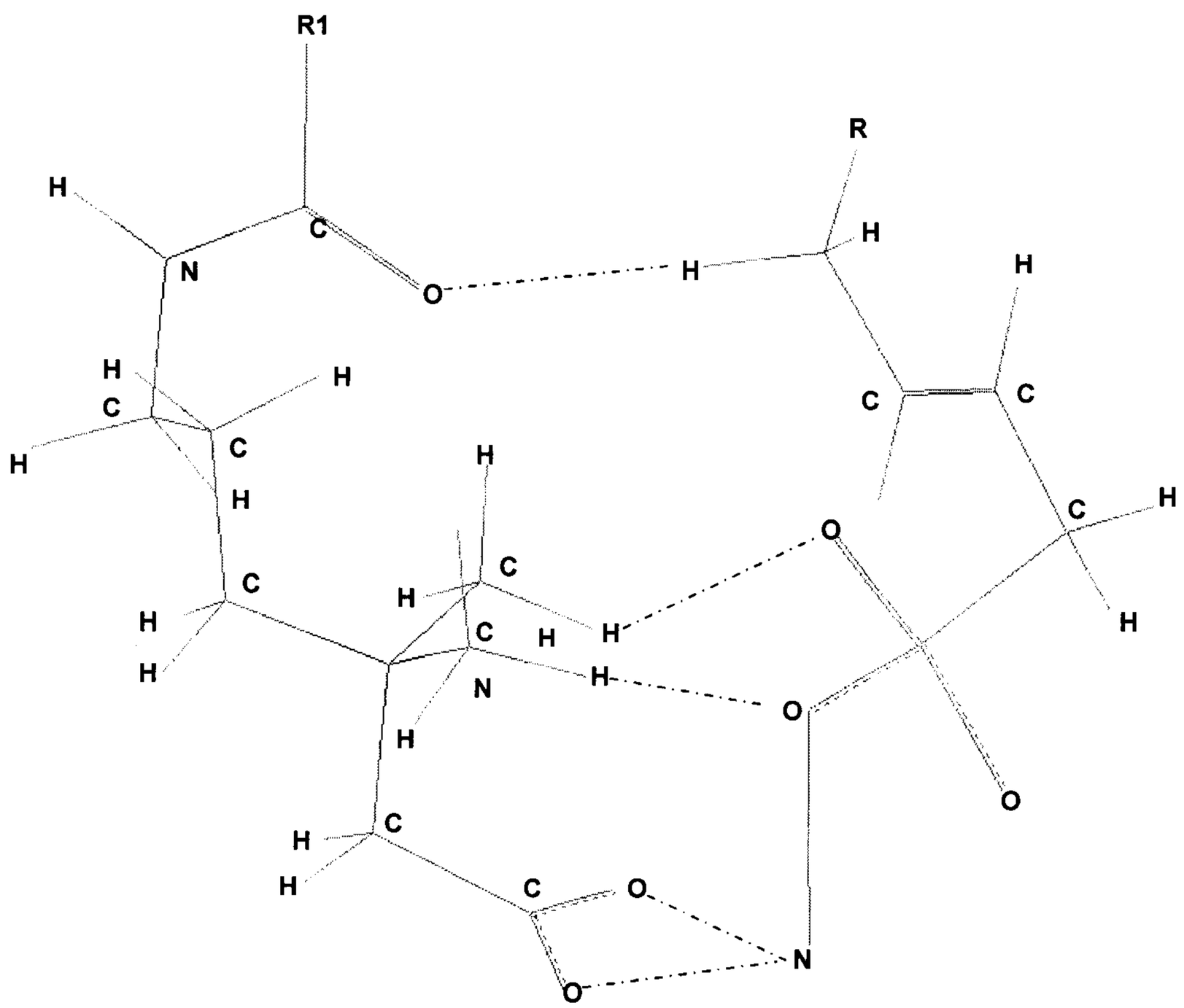
The present invention relates to the preparation of foaming formulations for high temperature, salinity and concentration of divalent ions, such as Calcium and Magnesium, that apply the synergistic effect of sodium alpha olefin sulfonates and alkyl amido propyl betaines; said inventions may use, as solvent, water, sea water, connate water, alcohols or mixtures all thereof. Said formulations control the piping of gas in reservoirs of the naturally fractured carbonate type.

FOAMING COMPOSITION FOR HIGH TEMPERATURE AND SALINITY

DESCRIPTION

TECHNICAL FIELD OF THE INVENTION

The present invention relates to a foaming composition with enhanced stability which controls the piping of gas in reservoirs of the naturally fractured carbonated type with high temperature and salinity conditions, by means the synergistic effect resulting from the supramolecular interaction of sodium alpha-olefin sulfonates with alkyl amido propyl betaines (1).



BACKGROUND OF THE INVENTION

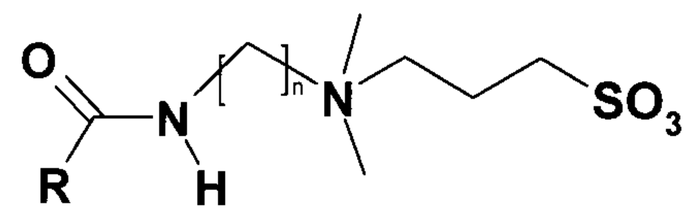
Foams are gas dispersions in a small amount of a liquid with a broad field of application at the industrial level. In the oil industry, the use of foams has been extended to naturally fractured reservoirs and their main application has been in controlling the advance of gas in exhausted wells close to the gas-oil contact zone, as well as in enhanced recovery processes. In these types of applications, the stability of the foam plays a major role, and it depends on the chemical structure of the surfactant used to generate it, as well as on the existing temperature, pressure and salinity conditions in the reservoir.

The main chemical families of surfactants that have been used to generate foams applied in enhanced recovery processes include: 1) Alkyl-aryl-sulfonates (US Patent 5,273,682), 2) Alkoxy-alkyl-benzene sulfonates (US Patent 5,049,311), 3) Alpha olefin sulfonates (US Patent 4,607,695), 4) Betaines (US Patent 7,104,327) and 5) Alkyl ether sulfates (Department of Energy of the United States of America DE-FC26-03NT15406 Report). However, when the temperature conditions within the reservoirs are elevated (higher than 70 °C), with salinity exceeding 30000 ppm total solids and the concentration of divalent ions, such as calcium and magnesium, is higher than 2000 ppm, the stability of the foam generated by this surfactant chemical families class decreases dramatically.

In order to increase the foams' stability and, hence, their tolerance to high concentrations of divalent ions and/or high temperature, formulations of foaming agents with enhanced properties have been developed, such as the following:

US Patent 3,939,911 describes a three surfactant system applied to enhanced recovery processes in high temperature reservoirs wherein the formation water contains from 200 to 14000 ppm of dissolved polyvalent ions, such as calcium and magnesium. The three surfactant system comprises: 1) Water-soluble salt of an alkyl or alkylaryl sulfonate wherein the alkyl chain may have from 5 to 25 carbon atoms, 2) A phosphate ester surfactant with an average molecular weight not to exceed 1000 AMU and 3) A sulfobetain-based surfactant having the structural formula (2) wherein R is an alkyl group having from 12 to 24 carbon atoms. The

combination is stable up to a temperature of at least 107 ºC and resistant to bacterial attack and inhibits scale formation.



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US Patent 4,703,797 refers to a method for sweep improvement during enhanced oil recovery processes. Said method concerns the generation of foam by the dispersion of the displacing liquid in an aqueous solution containing a surfactant formulation. The surfactant formulation comprises a lignosulfonate-based foaming agent and a surfactant foaming agent. The surfactant foaming agents disclosed include the group consisting of anionic, nonionic and amphoteric surfactants.

US Patent 5,295,540 refers to a foam-based method for improving oil production in subterranean formations comprising: 1) Injecting steam and liquids produced within the formation and 2) Injecting a mixture of steam, a noncondensible gas and an aqueous surfactant-polysaccharide mixture. The disclosed surfactants that may be used include linear toluene sulfonates, alkylaryl sulfonates, dialkykaril sulfonates, alpha olefin sulfonates and dimerized alpha olefin sulfonates.

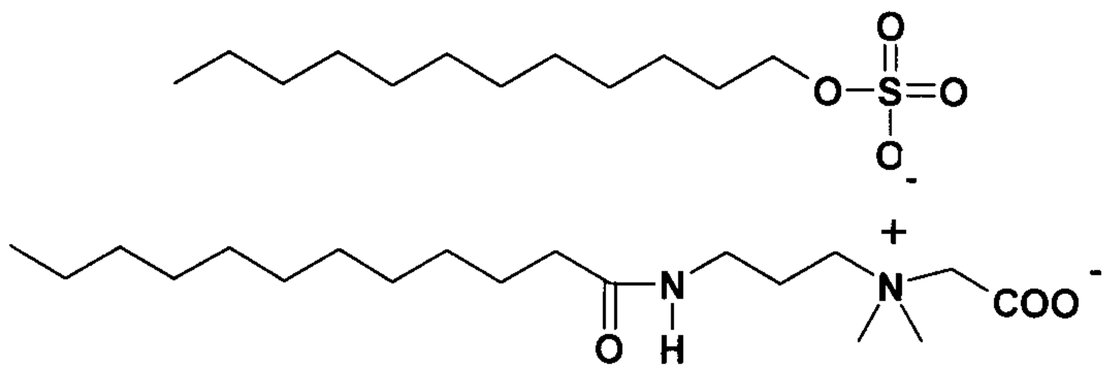
US Patent 5,542,474 refers to a foam-based method for improving the performance during the steam or carbon dioxide flood in subterranean, crude oil-containing formations comprising at least one production well and one injection well. In the oil recovery process, sweep efficiency through the delivery of steam is improved by: 1) Injecting steam until it starts appearing within the production well and 2) Thereafter, adding a mixture of steam, a noncondensible gas and an aqueous surfactant-polypeptide solution into the formation. The aqueous surfactant-polypeptide solution forms a stable foam with the formation oil at formation conditions. The surfactants used as the base for the foaming agent include sodium and ammonium salts of ethoxylated sulfated alcohols, linear alcohol ethoxylates and linear toluene sulfonates.

The paper "Improving the foam performance for mobility control and improved sweep efficiency in gas flooding" (*Ind. Eng. Chem. Res.* ***2004, 43,*** *4413-4421*) refers that the apparent stability and viscosity of an alpha olefin sulfonates-generated foam in brine with total concentrations of dissolved solids ranging from 30000 to 120000 ppm are substantially improved when formulated with partially hydrolyzed polyacrylamide-based polymers or biopolymers of the xanthan gum type. Moreover, the paper reports that the stability of foams generated by 12-carbon alpha olefin sulfonates is substantially increased when formulated with surfactants of the amine oxide type.

US Patent 7,104,327 provides methods for fracturing high temperature subterranean zones and foamed and viscous aqueous fracturing fluids therefor. The fracturing fluid of said invention comprises water, a terpolymer of 2-acrylamido-2-methylpropane-sulfonic acid, acrylamide and acrylic acid or salts thereof, a gas, a foaming agent and a viscosity breaker for controlling and reducing the viscosity of the fracturing fluid. The foaming agent in said invention is selected from the group consisting of C_8-C_{22} alkylamido-betaine, alpha olefin sulfonate, trimethyl-tallow-ammonium chloride, C_8-C_{22} alkylethoxylate sulfate and trimethyl-coco-ammonium chloride, and coco-amidopropyl betaine is specially mentioned as a foaming agent. Said invention never discloses using alkylamido-betaine and alpha olefin sulfonate mixtures to produce foams, or making use of the synergistic effect of the supramolecular complex thereof, which increases the stability of foams.

The synergistic effect of alkyl amido propyl betaines with anionic surfactants of the alkyl ether sodium sulfate and alkyl sodium sulfate type has been studied in the literature (*Langmuir* ***2000, 16,*** *1000-1013, Langmuir* ***2004, 20,*** *565-571, Langmuir* ***2004, 20,*** *5445-5453*), mainly indicating the alkyl amido propyl betaines ability to stabilize and enhance the rheological properties (viscosity) of foams generated by said anionic surfactants and that they can be applied in shampoos and hair conditioners. Additionally, the paper "Synergistic sphere-to-rod micelle transition in mixed solutions of sodium dodecyl sulfate and cocoamidopropyl betaine" (*Langmuir* ***2004, 20,*** *565-571*) indicates that the synergistic effect between

Cocoamidopropyl betaine and sodium dodecyl sulfate is due to an electrostatic attraction between both surfactants' heads (3).



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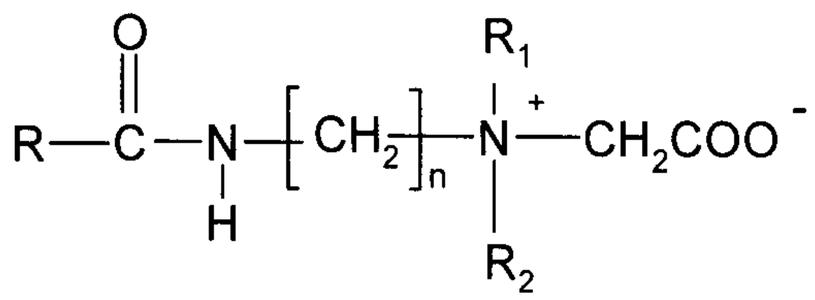
The patent application US 2007/0142235 A1 protects a composition and process for recovering oil, which consist in injecting an aqueous solution into a subterranean oil-bearing formation through one or more injection wells, displacing the solution into the formation, and recovering the oil from one or more production wells. The aqueous solution contains one or more amphoteric surfactants of the alkyl amido betaines type that form a viscoelastic surfactant gel that is able to reduce the interfacial tension and increase the viscosity of the injection fluid simultaneously in certain oils and brines. Viscoelastic gels are tolerant to electrolytes and multivalent cations, and are particularly useful within reservoirs characterized by medium to high temperatures, high salinity, high concentrations of divalent ions and low porosity. The application refers that the composition for recovering oil comprises one or more amphoteric surfactants selected for their ability to lower the interfacial tension and to increase viscosity simultaneously, an aqueous medium, a secondary surfactant and, optionally, one or more polymers to provide residual viscosity. The patent application indicates that one of the amphoteric surfactants (4), that the secondary surfactant can be selected from the anionic, cationic or non-ionic group, and that the polymer used to provide residual viscosity is selected from the polyacrylamide, partially hydrolyzed polyacrylamide, xanthan gum, hydroxyethyl cellulose or guar gum group. Moreover, the patent application refers that the combination of alkyl amido betaines with secondary surfactants of the linear sodium dodecylbenzene sulfonate and arylalkyl sodium xylene sulfonate type reduces interfacial tension and increases the viscosity of the system. The patent application does not refer using alkyl amido betaines-based amphoteric surfactants and mixtures thereof to generate foams, nor does it

disclose using mixtures of alkyl amido betaines and anionic surfactants of the alpha olefin sulfonates type.



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On the other hand, supramolecular chemistry is the part of chemistry that deals with the study of systems involving molecules or ions aggregates bound through non-covalent interactions, including electrostatic interactions, hydrogen bonds, π-π interactions, dispersion interactions and solvophobic effects. Supramolecular chemistry can be divided into two large areas: 1) Host-Guest Chemistry and 2) Self-assembly. The difference between these two large areas is a matter of size and form; where there is no significant difference in terms of size and none of the species acts as a host for the other, the non-covalent bond between two or more species is referred to as self-assembly.

From an energetic point of view, supramolecular interactions are much weaker than covalent interactions, which are located within the 150 to 450 Kj/mol energetic range for single bonds. The non-covalent interactions energetic interval ranges from 2 kj/mol for dispersion interactions to up to 300 kj/mol for ion-ion interactions (Table 1), and the sum of several supramolecular interactions can result in highly stable supramolecular complexes.

Table 1. Strength of Supramolecular Interactions

Interaction	Strength (Kj/mol)
Ion-ion	200-300
Ion-dipole	50-200
Dipole-dipole	5-50
Hydrogen bond	4-120
Cation-π	5-80
$\pi-\pi$	0-50
Van der Walls	< 5
Hydrophobic	Solvent-solvent interaction energy-related

Computational chemistry is a world-wide extensively used tool for predicting the stability and structure of chemical systems with enhanced potential properties and it has found its application at the industrial level in the development of structure-activity ratio quantitative studies. The computational calculation methods that have been used for this purpose include molecular mechanics methods, quantum methods, including semi-empirical and *ab initio* methods, as well as the density functional theory methods. As examples in the literature showing the use of computational chemistry for accurately predicting supramolecular interactions in chemical systems and/or chemical processes thermodynamic and kinetic aspects we can quote the papers: 1) Cornucopian Cylindrical Aggregate Morphologies from Self-Assembly of Amphiphilic Triblock Copolymer in Selective Media (*Journal of Physical Chemistry B*, ***2005,*** 109, 21549-21555), 2) Density Functional Calculations, Synthesis, and Characterization of Two Novel Quadruple Hydrogen-Bonded Supramolecular Complexes (*Journal of Physical Chemistry A*, ***2004,*** 108, 5258-5267), 3) Strong Decrease of the Benzene-Ammonium Ion Interaction upon Complexation with a Carboxylate Anion (*Journal of American Chemical Society*, ***1999***, 121, 2303-2306).

None of said references claims the use of foaming additives applying the synergistic effect of alpha olefin sodium sulfonates and alkyl amido propyl betaines for the development of formulations able to perform in high salinity and temperature environments. This invention presents the advantage of the generated formulations working efficiently in high salinity and temperature environments with high concentrations of calcium and magnesium divalent ions, and, furthermore, the generated foam shows superior stability compared to that generated by the currently used products worldwide.

BRIEF DESCRIPCTION OF THE INVENTION DRAWINGS

Next, a description of the contents of the present invention's figures:

Figure 1. Schematic diagram of the foam generation system, which allows for the foam stability to be assessed at atmospheric pressure and at up to 100 ºC. This system comprises the following elements: 1) Gas tank (GT), 2) foam meter (FM), 3) flow meter (F), 4) thermal bath (TB), 5) Video camera (VC), 6) Image capturing system (ICS), 7) Flow controlling valve (FCV), 8) Three-way valve (TWV) and 9) Valve.

Figure 2. Readings to be recorded during the foam stability test, where: TH=Total height, FH=Foam height and LH=Liquid height.

Figure 3. Necessary readings for the calculation of the foam stability.

Figure 4. Stability performance over time, at 1 kg/cm^2 and 75 ºC, of the foam prepared with brine at 1% by weight of molecular complexes **9**.

Figure 5. Stability performance over time, at 1 kg/cm^2 and 75 ºC, of the foam prepared with brine at 1% by weight of sodium dodec-2-en-1-sulfonate **10**.

Figure 6. Stability performance over time, at 1 kg/cm^2 and 75 ºC, of the foam prepared with brine at 1% by weight of coco-amido-propyl betaine **11**.

Figure 7. Stability over time, at 1 kg/cm^2 and 75 ºC, of the foams generated with different chemical products (supramolecular complexes **9**, sodium dodec-2-en-1-sulfonate **10**, and coco-amido-propyl betaine **11**) at 1% by weight.

Figure 8. Stability performance over time, at 1 kg/cm^2 and 75 ºC, of the foam prepared with brine at 1% by weight of formulation **A**.

Figure 9. Stability performance over time, at 1 kg/cm^2 and 75 ºC, of the foam prepared with brine at 1% of formulation **B**.

Figure 10. Stability performance over time, at 1 kg/cm^2 and 75 ºC, of the foam prepared with brine at 1% of formulation **C**.

Figure 11. Stability performance over time, of the foam at 1 kg/cm^2 and 75 ºC, prepared with brine at 1% of formulation **D**.

Figure 12. Stability over time, at 1 kg/cm^2 and 75 ºC, of the foams generated with different chemical products (formulation **A**, formulation **B**, formulation **C** and formulation **D**) at 1% by weight.

Figure 13. Stability performance over time, at 1 kg/cm^2 and 75 ºC, of the foam prepared with brine at 1% by weight of supramolecular complexes **9**.

Figure 14. Stability performance over time, at 1 kg/cm^2 and 75 ºC, of the foam prepared with brine at 1% by weight of formulation **E**.

Figure 15. Stability performance over time, at 1 kg/cm^2 and 75 ºC, of the foam prepared with brine at 1% of formulation **F**.

Figure 16. Stability over time, at 1 kg/cm^2 and 75 °C, of the foams generated with different chemical products (supramolecular complexes **9**, formulation **E** and formulation **F**) at 1% by weight.

Figure 17. Stability performance over time, at 1 kg/cm^2 and 75 ºC, of the foam prepared with brine at 1% by weight of supramolecular complexes **9**.

Figure 18. Stability performance over time, at 1 kg/cm^2 and 75 ºC, of the foam prepared with brine at 1% by weight of formulation **E**.

Figure 19. Stability performance over time, at 1 kg/cm^2 and 75 ºC, of the foam prepared with brine at 1% of formulation **F**.

Figure 20. Stability over time, at 1 kg/cm^2 and 75 °C, of the foams generated with different chemical products (supramolecular complexes **9**, formulation **E** and formulation **F**) at 1% by weight.

Figure 21. Stability performance over time, at 1 kg/cm^2 and 75 ºC, of the foam prepared with brine at 1% by weight of supramolecular complexes **9**.

Figure 22. Stability performance over time, at 1 kg/cm^2 and 75 ºC, of the foam prepared with brine at 1% by weight of formulation **G**.

Figure 23. Stability over time, at 1 kg/cm^2 and 75 °C, of the foams generated with different chemical products (supramolecular complexes **9** and formulation **G**) at 1% by weight.

Figure 24. PVT cell adapted and used for the foams stability test at high pressure and temperature, where: BPR = Pressure regulating valve.

Figure 25. Stability performance at 100 kg/cm^2 and 95 ºC over time, of the foam formed with brine at 1% in weight of molecular complexes **9**.

Figure 26. Stability performance at 100 kg/cm^2 and 95 ºC over time, of the foam formed with brine at 1% by weight of sodium dodec-2-en-1-sulfonate **10**.

Figure 27. Stability performance at 100 kg/cm^2 and 95 ºC over time, of the foam formed with brine at 1% by weight of coco-amido-propyl betaine **11**.

Figure 28. Stability over time, at 100 kg/cm^2 and 95 °C, of the foams generated with different chemical products (supramolecular complexes **9**, dodec-2-en-1-sodium sulfonate **10** and coco-amido-propyl betaine **11**) at 1% by weight.

Figure 29. Experimental array used for the control of gas piping, where CP1= Computerized pump for injection, CP2= Computerized pump for injection, CP3 = Computerized pump for overpressure, V1 to V15 = Shut-off valves, IP = Pressure gauge; PC = Packed column, TC1 = Input visual cell; TC2 = Output visual cell and BPR= Pressure regulation valve.

Figure 30. Artificial longitudinal fracture used for the gas piping control test.

Figure 31. Diagram showing the foam in a longitudinal fracture, where said foam is observed to resist a 10 psi pressure difference after two weeks.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to the synergistic effect resulting from the supramolecular interaction of sodium alpha-olefin sulfonates with alkyl amido propyl betaines and its application in the development of enhanced-stability foaming formulations for the control of gas piping in reservoirs of the naturally fractured carbonate type with high salinity and temperature conditions.

The supramolecular complexes developed from the interaction of sodium alpha olefin sulfonates with alkyl amido propyl betaines show tolerance under high temperature and/or pressure conditions to the presence of divalent ions such as calcium and magnesium and, when used in formulations, they generate stable

foams under such conditions, largely surpassing, in terms of performance as foaming agents, the sodium alpha olefin sulfonates or alkyl amido propyl betaines-based compounds traditionally used as foaming agents in formulations at the industrial level in low temperature processes and in brines with low concentrations of divalent ions.

The development of the present invention followed a procedure involving the following steps: 1) Molecular design through computational chemistry, 2) Supramolecular complexes synthesis, 3) Spectroscopic characterization of the supramolecular complexes and 4) Experimental assessment of the supramolecular complexes foaming properties. The selection of the present methodology is based on the fact that the key point in order to solve the problems of generating stable foams in brines with high concentrations of divalent ions and at high temperature and pressure conditions relies on the understanding, at the molecular level, on how to control the cationic exchange reaction between the foaming agent and the divalent ions under specific conditions.

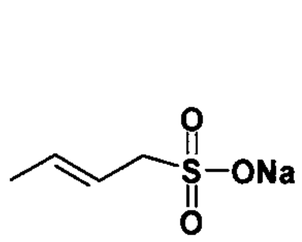
1) MOLECULAR DESIGN THROUGH COMPUTATIONAL CHEMISTRY

Before going into detail, and for clarification purposes, we should mention that currently, before engaging in the synthesis of a new compound or complex, it is customary to design, using theoretical calculations, a molecule by means of which to attempt solving a specific problem, and we did this the way we explain next.

Once established this, the first thing that is important pointing out is that the literature mentions that compounds of the alpha olefin sulfonates type may be used for the generation of foams at high temperatures and in brines with dissolved solids total concentrations from 30000 and 120000 ppm and whose divalent ions concentrations range from 2000 to 3800 ppm (*Industrial & Engineering Chemistry Research* ***2004, 43,*** *4413-4421*). Additionally, the stability of the generated foam depends drastically on the concentration of divalent ions, since the exchange of sodium ions for calcium or magnesium ions is thermodynamically favored, and

alpha olefin sulfonates with divalent ions, which are compounds without foaming properties, are generated. On the other hand, the literature indicates that one way of increasing the viscosity of solutions that use sodium alkyl sulfates as foaming agents is through the use of coco amido propyl betaine, and that the mechanism driving such increase is through an electrostatic interaction between both surfactants' heads (*Langmuir* ***2004, 20,*** *565-571*). Furthermore, the fact that betaines have a high electronic density carbonyl group can result in the alpha olefin sulfonates' sodium atom strongly coordinating with said group, thus reducing the calcium or magnesium ions exchange rate at high temperatures in brines with high concentrations of stable ions, hence obtaining a more stable foam. Moreover, alkyl amido propyl betaines possess, in their structure, an amido group that is highly susceptible to supramolecularly interact with the alpha olefin sulfates allylic protons and thus considerably increasing the stability of the generated supramolecular complexes.

Theoretical calculations with the method *ab initio* and the set of 321-G bases were used in order to optimize the geometry in the gas phase and to determine the total energy and Mulliken atomic charges of sodium alpha olefin sulfonate- and alkyl-amidopropyl betaines-based compounds and supramolecular compounds derived from the interaction thereof. The structural formulas (5) of sodium but-2-en1-sulfonate (alpha olefin sulfonate) **1**, ethyl-amido-propyl-betaine (alkyl-amido propyl betaine) **2** and supramolecular compound **3** derived from the interaction of said two compounds. Additionally, tables 2, 3 and 4 show the energetic results, the bonding distances and the main Mulliken atomic charges for said compounds and the corresponding supramolecular complex.



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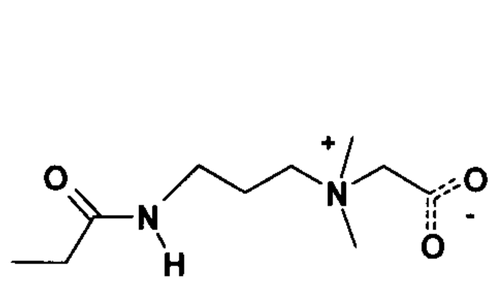

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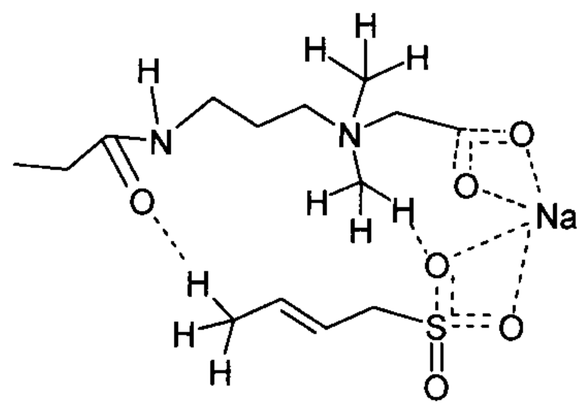

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Table 2. Energy of compounds **1** y **2** and of supramolecular complex **3** obtained with the 321-G base.

Compound or Complex	321-G base	
	Total energy (kJ/moL)	Interaction Energy (kJ/moL)
1	-2,450,677.36	
2	-1,887,922.90	
3	-4,338,844.63	-244.37

Wherein:

1 = sodium but-2-en-1-sulfonate

2 = ethyl-amido-propyl-betaine

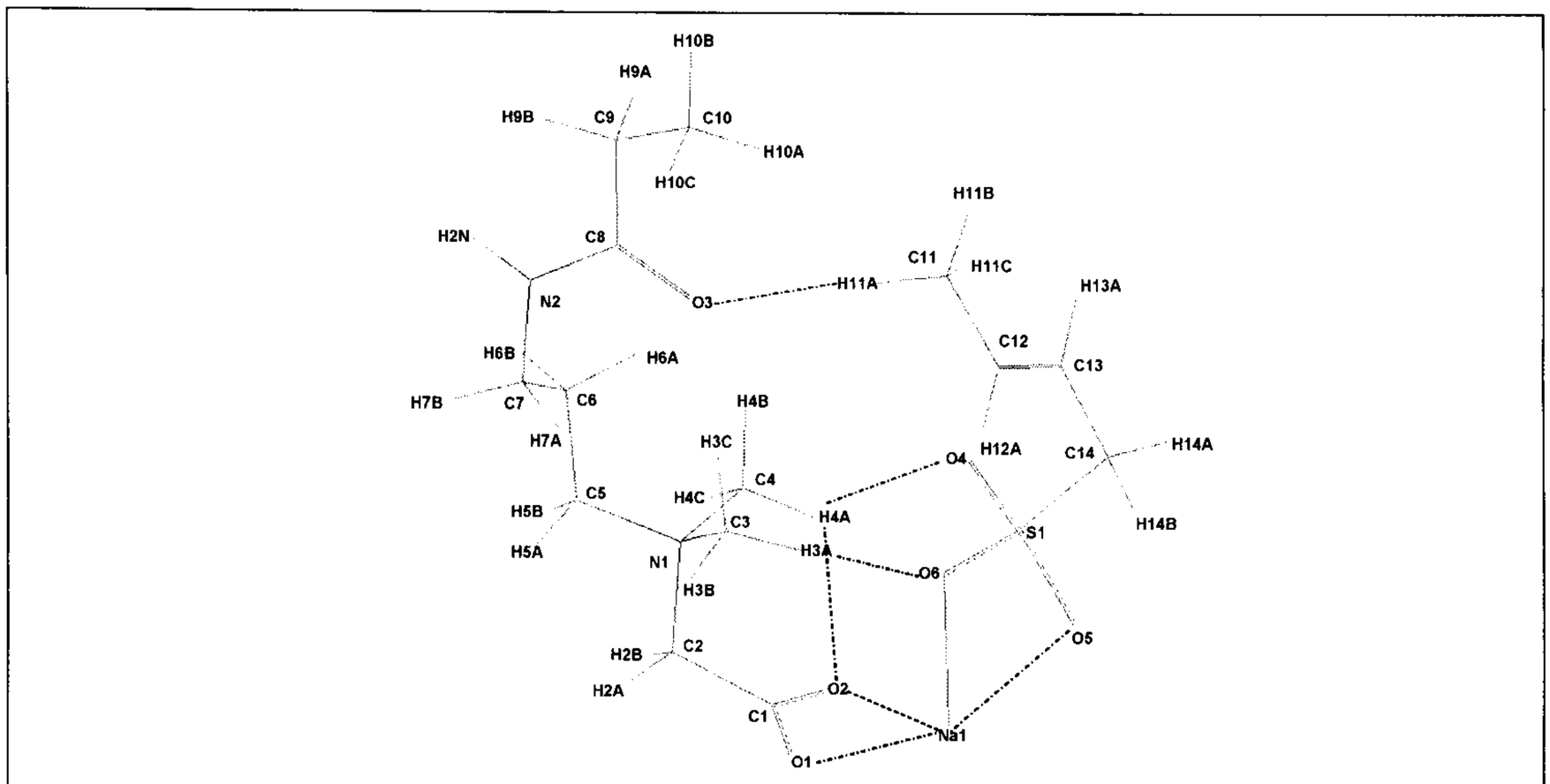
3 = Supramolecular complex derived from the interaction between sodium but-2-en-1-sulfonate and ethyl-amidopropyl-betaine

The analysis of table 2 results shows that the formation of supramolecular complex **3** from compounds **1** and **2** interactions is strongly favored from a thermodynamic point of view. Furthermore, the -244.1 kj/moL interaction energy indicates the presence of ion-ion-type supramolecular interactions, or a combination of ion-dipole and hydrogen bonds interactions.

The analysis of Table 3 results shows that the 2.289, 2.248, 2.282 and 2.311 Å distances for the **O1···Na1, O2···Na1, O5···Na1 and O6···Na1** interactions are lower than the Van der Waals Radiuses sum for the oxygen (Van der Waals Radius of 1.40 Å) and sodium atoms (Van der Waals Radius of 2.31 Å) and are typical from structures containing coordination bonds **Na-O** and sulfonate groups (*Crystal Growth & Design* **2006,** 6[2], 514-518) or carbonyl groups (*Green Chemistry* **2005**, 7, 716-720). Moreover, the 1.991 and 2.277 Å bonding distances

for the **H3A···O6** and **H4A···O4** interactions show the presence of two strong hydrogen bonds, which, together with the coordination bonds formed by the sodium atom are responsible for the formation of supramolecular complex **3**. Additionally, the 2.490 Å bonding distance for the **H11A···O3** interaction indicates the presence of a supramolecular interaction between the alpha olefin sulfonates allylic protons and the alkyl amido propyl betaine group oxygen atom.

Table 3 Main bonding distances in compounds 1, 2 and in supramolecular complex 3.



Bond or interaction distance	Compound or complex bonding distance (Å)		
	1	2	3
O1···Na1			2.289
O2···Na1			2.248
O5···Na1	2.161		2.282
O6···Na1	2.164		2.311
H3A···O6			1.991
H4A···O4			2.277
H11A···O3			2.490
C1:::O1		1.242	1.251
C1:::O2		1.244	1.254
S1-O4	1.570		1.576

S1-O6	**1.603**		**1.602**
S1-O5	**1.602**		**1.595**

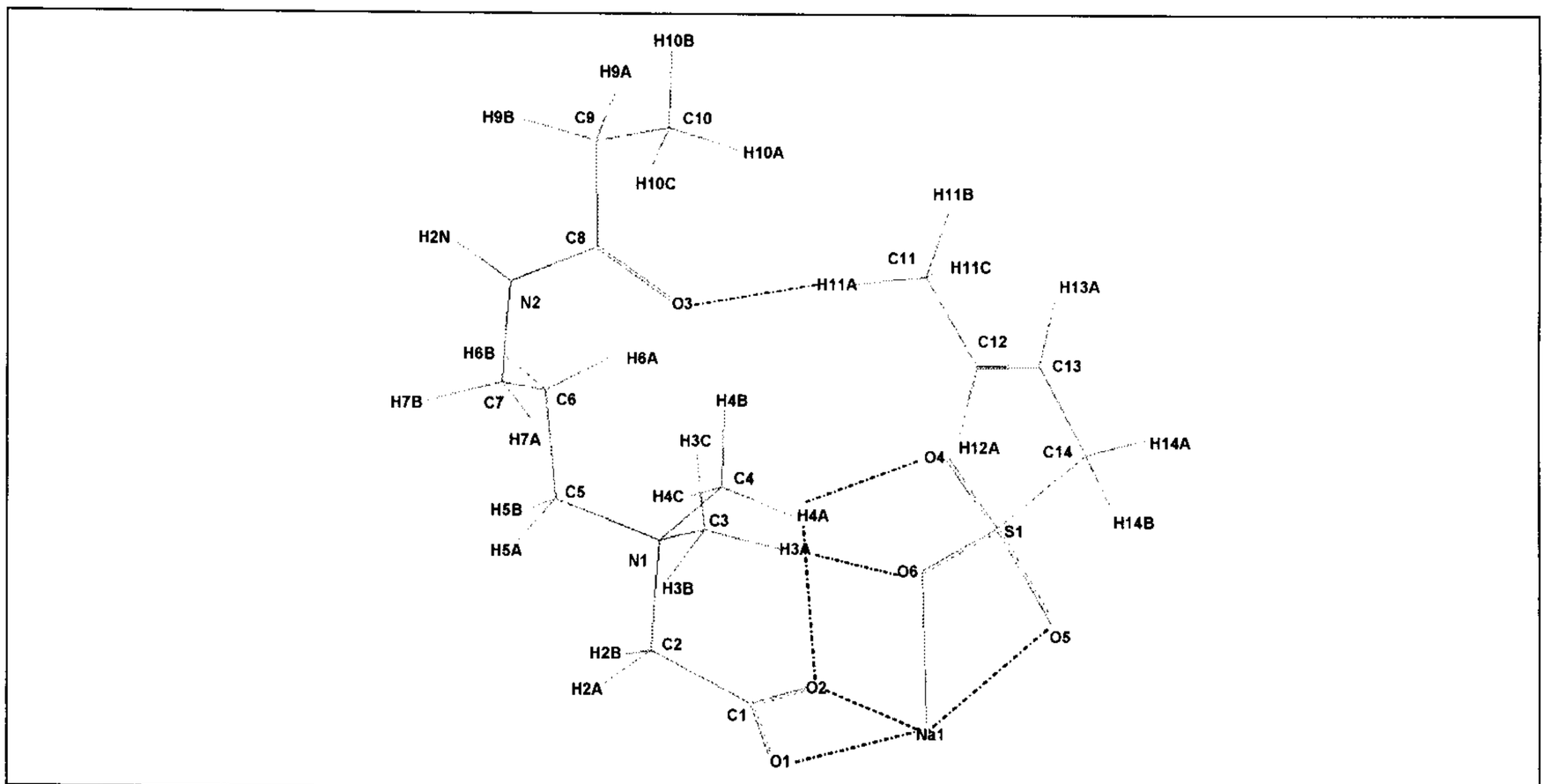
Wherein:

1 = sodium but-2-en-1-sulfonate

2 = ethyl-amido-propyl-betaine

3 = Supramolecular complex derived from the interaction between sodium but-2-en-1-sulfonate y ethyl-amido-propyl-betaine

Table 4 Mulliken atomic charges of compounds 1, 2 and supramolecular complex 3.



Atom	Compound or complex atomic charge (e)		
	1	2	3
C1		0.846	0.844
C2		-0.317	-0.284
C3		-0.427	-0.506
C4		-0.424	-0.428
C5		-0.176	-0.188
C6		-0.479	-0.477
C7		-0.144	-0.158
C8		0.895	0.910
C9		-0557	-0.550
C10		-0.567	-0.579
C11	-0.634		-0.660

C12	-0.206		-0.184
C13	-0.233		-0.238
C14	-0.833		-0.879
O1		-0.720	-0.714
O2		-0.723	-0.710
O3		-0.645	-0.648
O4	-0.733		-0.760
O5	-0.828		-0.792
O6	-0.833		-0.816
N1		-0.748	-0.747
N2		-0-909	-0.906
Na1	0.678		0.528
S1	1.895		1.897
H2A		0.252	0.265
H2B		0.248	0.265
H3A		0.337	0.381
H3B		0.245	0.234
H3C		0.231	0.287
H4A		0.340	0.373
H4B		0.228	0.245
H4C		0.233	0.227

H5A		**0.261**	**0.258**
H5B		**0.248**	**0.249**
H11A		**0.231**	**0.264**
H12A	**0.262**		**0.236**
H13A	**0.250**		**0.257**
H14A	**0.298**		**0.290**
H14B	**0.304**		**0.297**

Wherein:

1 = sodium but-2-en-1-sulfonate

2 = ethyl-amido-propyl-betaine

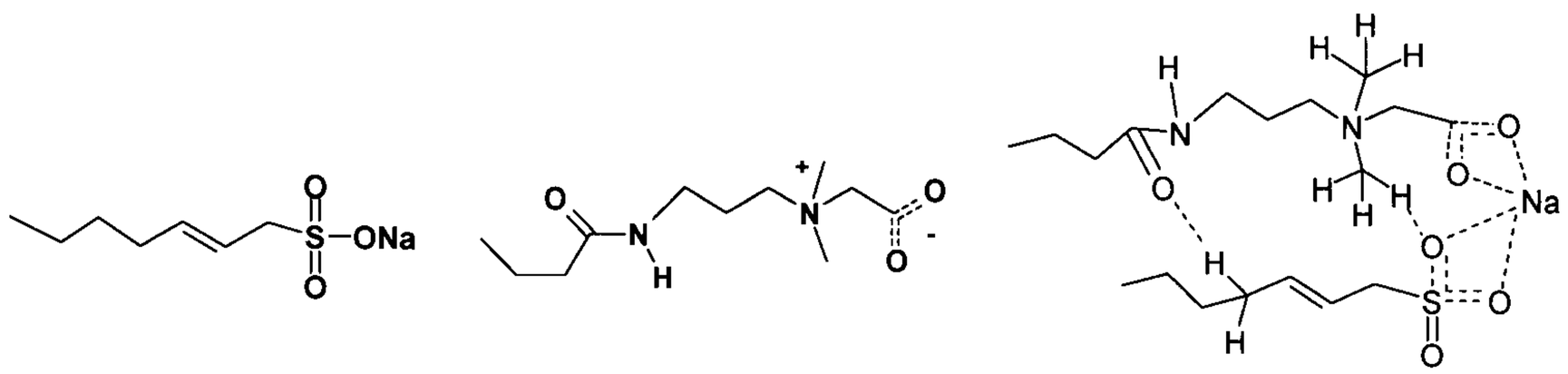
3 = Supramolecular complex derived from the sodium but-2-en-1-sulfonate and ethyl-amido-propyl-betaine interaction

The analysis of Table 4 results shows that the Mulliken atomic charge on supramolecular complex **3** sodium atom **Na1** is reduced by 0.15 units with respect to the charge that this atom has in the sodium alpha olefin sulfonate compound **1**, whereas oxygen atoms **O1** and **O2** atomic charges undergo a 0.006 and 0.013 units decrease, with respect to those in alkyl amidopropyl betaine **2**. This significant change in the Mulliken atomic charges confirms that in supramolecular complex **3**, the **Na1** sodium atom is coordinated with oxygen atoms **O1** and **O2**.

Additionally, the Mulliken atomic charge on supramolecular complex **3** hydrogen atoms **H3A** and **H4A** increases by 0.027 and 0.033 units, respectively, with respect to the charges shown by these atoms in alkyl amidopropyl betaine compound **2**, whereas oxygen atom **O4** Mulliken atomic charge undergoes a 0.0027 units increase, and that of oxygen atom **O6** undergoes a 0.017 decrease, with respect to sodium alpha olefin sulfonate compound **1**. This significant change

in the Mulliken atomic charges confirms the occurrence of non-conventional hydrogen bonds in supramolecular complex **3**, which are widely recognized for generating an energetic stabilization maximum level in supramolecular complexes (*Account Chemical Research*, **1996**, 29, 441-449 and *Crystal Growth & Design*, **2003,** 3, 239-246).

In order to establish the effect of the length of the alkyl amido propyl betaines and sodium alpha olefin sulfonates hydrophobic chains on the stability of the supramolecular complexes formed, by means of computational chemistry, and using the sodium hept-2-en-1-sulfonate (sodium alpha olefin sulfonate) **4** and propyl-amido-propyl-betaine (alkyl amidopropyl betaine) **5** interaction, supramolecular complex **6** was designed (6).



(6)

Tables 5 and 6 show the energetic results and the main bonding distances for compounds **4**, **5** and supramolecular complex **6**.

Table 5. Energy of compounds **4**, **5** and supramolecular complex **6** obtained with the 321-G base.

Compound or Complex	**321-G Base**	
	Total energy (kJ/moL)	**Interaction Energy (kJ/moL)**
4	-2,756,145.74	
5	-1,989,745.37	

6	-4,746,129.56	-238.45

Wherein:

4 = sodium hept-2-en-1-sulfonate

5 = propyl-amido-propyl-betaine

6 = Supramolecular complex derived from the sodium hept-2-en-1-sulfonate and propyl-amido-propyl-betaine interaction.

The analysis of table 5 results shows that the formation of supramolecular complex **6** from the interaction between compounds **4** and **5** is strongly favored from a thermodynamic point of view. Additionally, the -238.45 kj/moL interaction energy is in the same order of magnitude as the one obtained for supramolecular complex **3**; hence, we can infer that the supramolecular complexes' hydrophobic part does not contribute significantly to the thermodynamic stability thereof, and that it mainly impacts on the solubility properties and the capability of generating the maximum amounts of foam at a lesser concentration of the supramolecular complexes (critical micelle concentration).

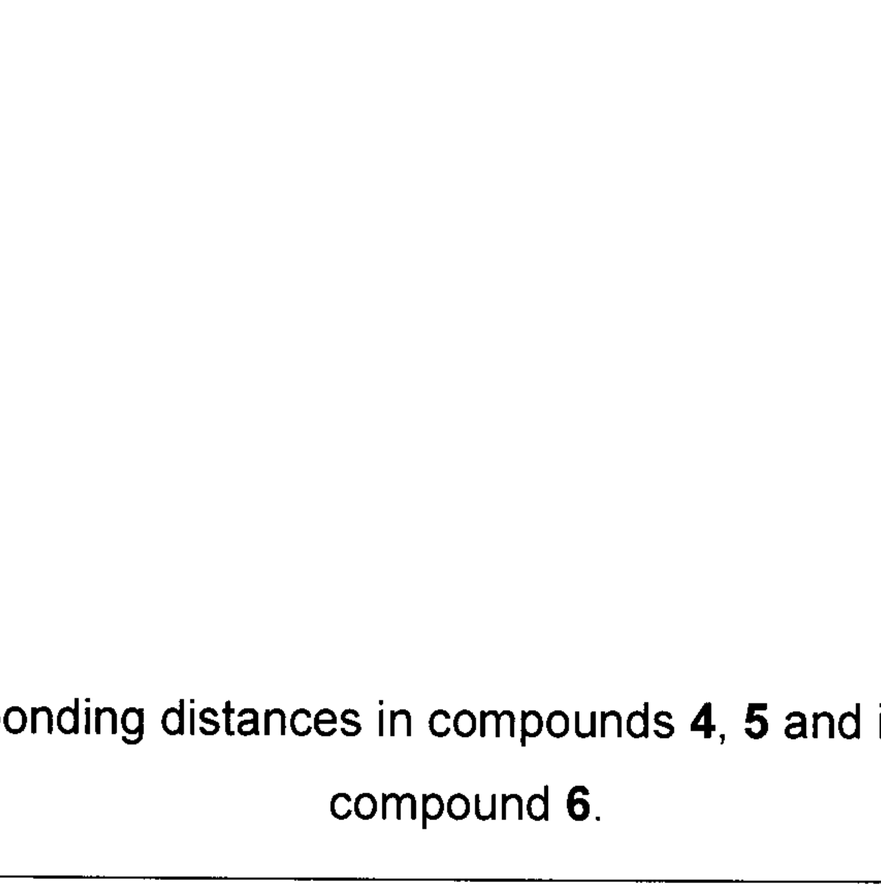
The analysis of Table 6 results shows that the bonding distances obtained for **O1···Na1, O2···Na1, O5···Na1, O6···Na1, H3A···O6, H4A···O4 and H15A···O3** interactions are in the same order of magnitude than those obtained for supramolecular complex **6**, thus confirming that the hydrophobic moiety does not significantly contribute to the stability of the supramolecular complexes obtained from the interaction between sodium alpha olefin sulfonate and alkyl amido propyl betaines.

2) SUPRAMOLECULAR COMPLEXES SYNTHESIS

The supramolecular complexes derived from the present invention are obtained according to the synthesis procedure (7), which consists in mixing, at room temperature and atmospheric pressure, sodium alpha olefin sulfonates **7** with alkyl

amidopropyl betaines **8**. The molar ratio at which the supramolecular complexes are formed from the sodium alpha olefin sulfonates with alkyl amido propyl betaines interaction ranges from 1 to 2 or from 2 to 1, with the molar ratio 1 to 1 being preferred.

Table 6 Main bonding distances in compounds **4**, **5** and in supramolecular compound **6**.



Bonding or interaction distance	Compound or complex bonding distance (Å)		
	1	2	3

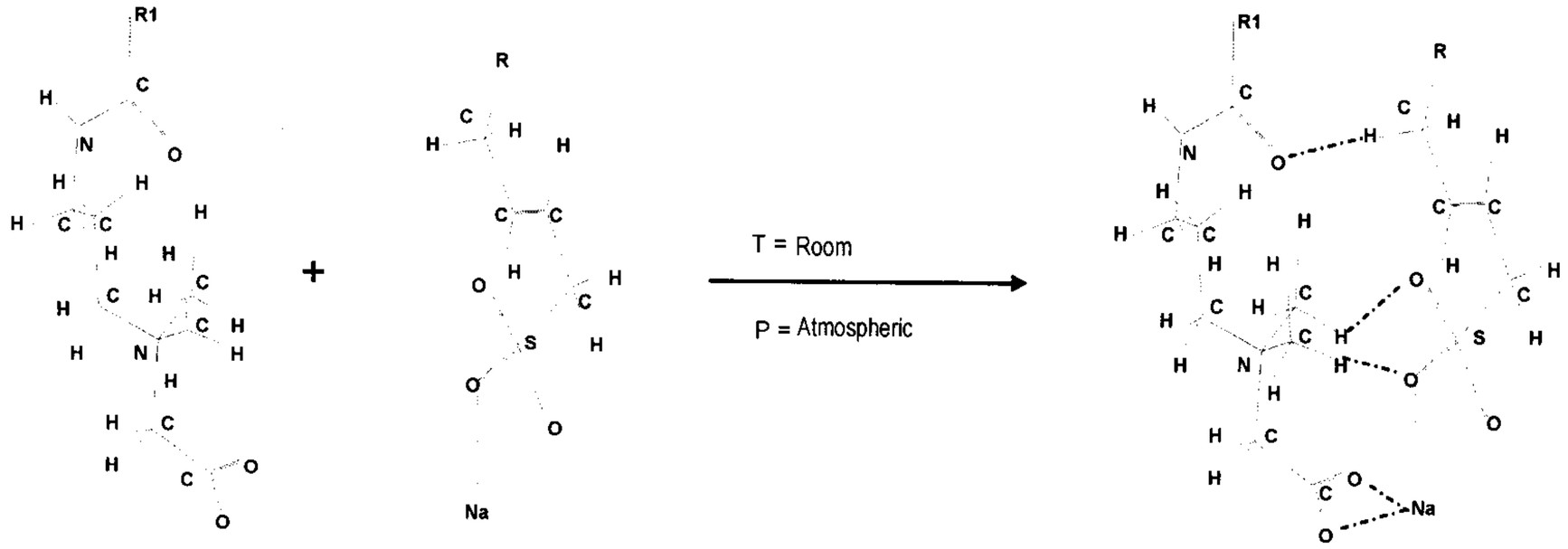
O1···Na1			2.295
O2···Na1			2.248
O5···Na1	2.161		2.298
O6···Na1	2.164		2.298
H3A···O6			1.967
H4A···O4			2.309
H15B···O3			2.577
C1:::O1		1.242	1.251
C1:::O2		1.244	1.254
S1-O4	1.570		1.576
S1-O6	1.603		1.598
S1-O5	1.602		1.594

Wherein:

1 = sodium but-2-en-1-sulfonate

2 = ethyl-amido-propyl-betaíne

3 = Supramolecular complex derived from the interaction between sodium but-2-en-1-sulfonate and ethyl-amido-propyl-betaine.



Alkyl amido propyl betaine

Sodium alpha olefin sulfonate

Supramolecular complexes

(i)

The formation of the supramolecular complexes from the mixture of sodium alpha olefin sulfonates with alkyl amido propyl betaines may be carried out in water, alcohols or a water-alcohols mixture, with the aqueous medium being preferred. The supramolecular complexes final concentration by weight can range from 0.1% to 50%, preferably within the range of 20% to 50%.

The sodium alpha olefin sulfonates useful for the present invention include sodium but-2-en-1-sulfonate, sodium pent-2-en-1-sulfonate, sodium hex-2-en-1-sulfonate, sodium hept-2-en-1-sulfonate, sodium oct-2-en-1-sulfonate, sodium non-2-en-1-sulfonate, sodium dec-2-en-1-sulfonate, sodium undec-2-en-1-sulfonate, sodium dodec-2-en-1-sulfonate, sodium tetradec-2-en-1-sulfonate, sodium hexadec-2-en-1-sulfonate and the mixture of one or more of said sodium alpha olefin sulfonates. The alkyl amido propyl betaines that are useful for the present invention include ethyl-amydo-propyl-betaine, propyl-amido-propyl-betaine, butyl-amido-propyl-betaine, pentyl-amido-propyl-betaine, hexyl-amido-propyl-betaine, heptyl-amido-propyl-betaine, octyl-amido-propyl-betaine, nonyl-amido-propyl betaine, decyl-amido-propyl betaine, undecyl-amido-propyl betaine, coco-amido-propyl betaine and mixtures of two or more of these alkyl amido propyl betaines.

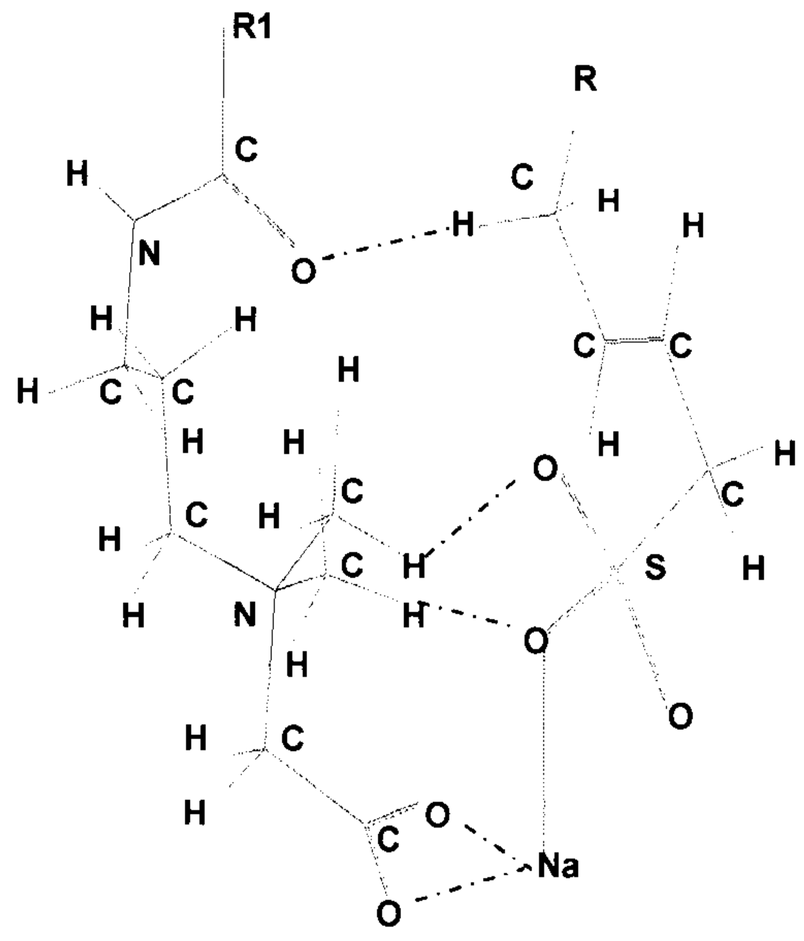
The following examples will serve to illustrate the synthesis of the two supramolecular complexes that are the subject matter of the present invention, whose formulas and chemical nature are also detailed below (Examples 1 and 2), and below we also detail the composition and effectiveness of said complexes that, briefly, consist in the combination supramolecular complexes derived from the interaction between sodium olefin sulfonates and alkyl amido propyl betaines with: anionic surfactants (Example 7) itaconic acid-derived oligomers (Example 8), acrylamide and acrylic acid-derived copolymers (Example 9), itaconic acid-derived oligomers and acrylamide and acrylic acid-derived copolymers (Example 10), cationic surfactants (Example 12), cationic surfactants and itaconic acid-derived

oligomers (Example 13), etc. Additionally, examples are shown were these complexes are used together with different gases in order to generate the foam.

Example 1

Synthesis of supramolecular complexes **9** resulting from the interaction between sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl betaine **11**.

In a 1000 mL two-neck round bottom flask, equipped with a magnetic stirrer and a thermometer, 300 grams of an aqueous solution containing 30.4% by weight (0.2719 moL) of coco-amido-propyl-betaine **11** and 200 grams of an aqueous solution containing 33.8% by weight (0.2719) of sodium dodec-2-en-1-sulfonate **10** were mixed at room temperature and atmospheric pressure, stirring vigorously. The mixture was stirred vigorously for 3 hours and then the solvent was evaporated, yielding 158.4 grams of a dark brownish doughy solid containing the supramolecular complexes **9** (whose structural formula is shown in (8), where R is radical $-C_8H_{17}$ y R_1 which is constituted by a group of radicals comprising $-C_{11}H_{23}$, $-C_9H_{19}$ y C_7H_{15}).

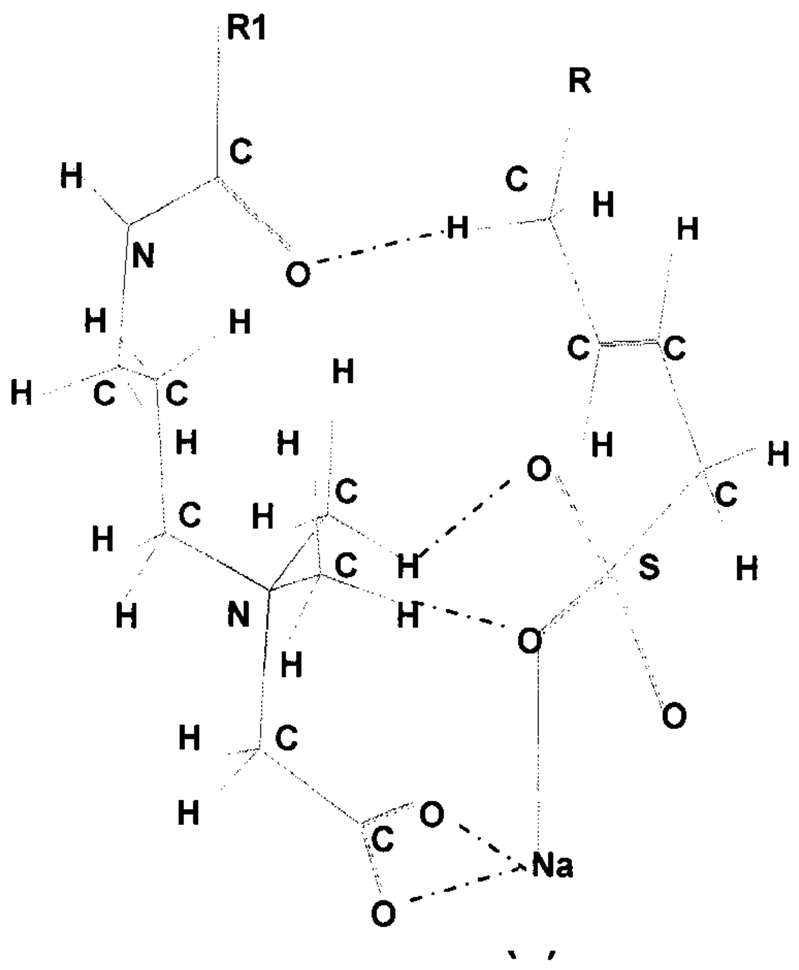


(8)

Example 2

Synthesis of supramolecular complexes **12** resulting from the interaction of sodium tetradec-2-en-1-sulfonate **13** and sodium hexadec-2-en-1-sulfonate **14** with coco-amido-propyl betaine **11**.

In a 1000 mL two-neck round bottom flask, equipped with a magnetic stirrer and a thermometer, 300 grams of a solution containing 50.0% by weight of water, 16.6% by weight of ethanol and 31.7% by weight (0.2836 moL) of coco-amido-propyl-betaine **11** were mixed at room temperature and atmospheric pressure, stirring vigorously, with 200 grams of an aqueous solution containing 28.2% by weight (0.2041 moL) of sodium tetradec-2-en-1-sulfonate **13** and 12.1% by weight (0.0795 moL) of sodium hexadec-2-en-1-sulfonate **14**. The mixture was stirred vigorously for 3 hours, and then the solvent was evaporated, yielding 174.4 grams of supramolecular complexes **12** (whose structural formula is shown in (9), wherein R is constituted by a group of radicals comprising $-C_{10}H_{21}$ and $-C_{12}H_{25}$, and R_1 is constituted by a group of radicals comprising $-C_{11}H_{23}$, $-C_9H_{19}$ y $-C_7H_{15}$) as a dark brownish doughy solid.

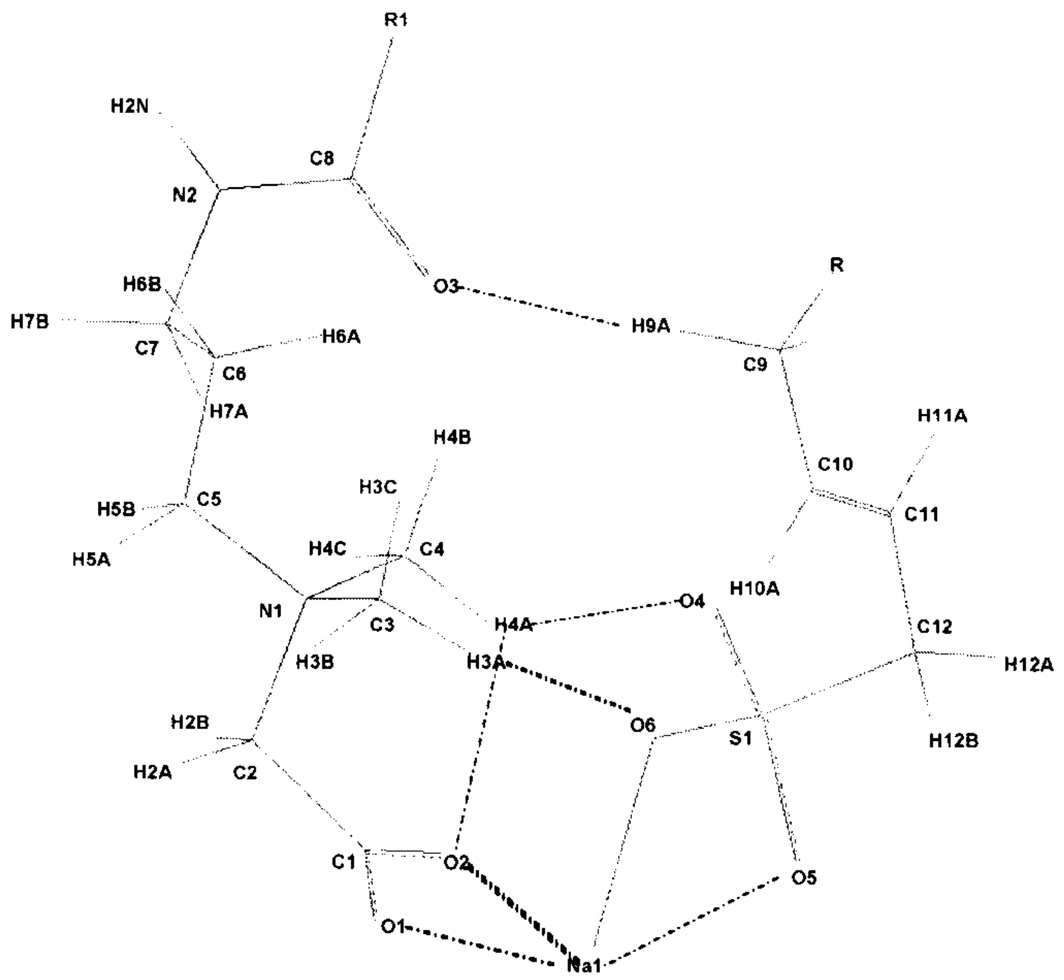


3) SUPRAMOLECULAR COMPLEXES SPECTROSCOPIC CHARACTERIZATION

Example 3

Spectroscopic characterization of sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl-betaine **11** interaction-derived supramolecular complexes **9** by ^{1}H and ^{13}C Nuclear Magnetic Resonance and Infrared Spectroscopy.

In the ^{1}H nuclear magnetic resonance spectrum of supramolecular complexes **9** (10) obtained in deuterated water, the following characteristic signals are observed: 1) a single signal for methylic protons **H3** and **H4** at 3.06 ppm and 2) a single signal for methylenic protons **H2** at 3.71 ppm; whereas in the ^{1}H nuclear magnetic resonance spectrum of coco-amido-propyl betaine **11** a single signal is observed for methylic protons **H3** and **H4** at 3.01 ppm and the single signal for the methylenic protons **H2** at 3.66 ppm. The lack of protection suffered by the methylic protons **H3** and **H4** and methylenic protons **H2** in supramolecular complexes **9** with respect to those in coco-amido-propyl betaine **11** indicates the presence of interactions that generate the supramolecular complexes.



(10)

The following characteristic signals are observed in the supramolecular complexes ^{13}C nuclear magnetic resonance spectrum: 1) a main single signal for the amido

carbonyl group carbon **C8** at 175.9 ppm, 2) a main simple signal for the carbonyl group carbon **C1** of sodium salt at 169.3 ppm, 3) two main simple signals for the alkenylic carbon **C10** at 138.1 and 13.6.0 ppm, 4) two main simple signals for the alkenylic carbon **C11** at 119.7 and 119.2 ppm, 5) three main simple signals for methylenic carbons **C5** at 64.0, 63.1 and 62.5 ppm, 6) a main simple signal for methylenic carbon **C12** at 55.0 ppm, 7) a simple signal for methylic carbons **C3** and **C4** at 50.9 ppm and 8) a simple signal for methylenic carbon **C9** at 36.2 ppm. A comparison of the chemical shifts obtained in the supramolecular complexes **9** ^{13}C nuclear magnetic resonance spectrum with those obtained in the coco-amido-propyl betaine **11** and sodium dodec-2-en-1-sulfonate **10** ^{13}C nuclear magnetic resonance spectra, shows the following: 1) the main simple signals for the carbonyl carbons **C8** and **C9** are observed in the supramolecular complexes **9** ^{13}C spectrum at 175.9 and 169.3 ppm, whereas in the coco-amido-propyl betaine **11** ^{13}C spectrum these are observed at 175.8 and 168.8 ppm, 2) the main simple signals for alkenylic carbons **C10** and **C11** are observed in the supramolecular complexes **9** ^{13}C spectrum at 138.1, 136.0, 119.7 and 119.2 ppm, whereas in the dodec-2-en-1-sodium sulfonate **10** ^{13}C spectrum these are observed at 138.7, 136.6, 119.2 and 118.6 ppm, 3) the main simple signals for methylenic carbons **C5** are observed in the supramolecular complexes **9** ^{13}C spectrum at 64.0, 63.1 and 62.5 ppm, whereas in the coco-amido-propyl betaine **11** ^{13}C spectrum these are observed at 63.9, 62.6 and 62.1 ppm, 4) a main simple signal for methylenic carbon **C12** is observed in the supramolecular complexes **9** ^{13}C spectrum at 55.0 ppm, whereas in the sodium dodec-2-en-1-sulfonate **10** ^{13}C spectrum it is observed at 54.9 ppm, 5) a main single simple for methylic carbons **C3** and **C4** is observed in the supramolecular complexes **9** ^{13}C spectrum at 50.9 ppm, whereas in the coco-amido-propyl betaine **11** ^{13}C spectrum it is observed at 51.4 ppm, 6) a main simple signal for methylenic carbon **C9** is observed in the supramolecular complexes **9** ^{13}C spectrum at 36.2 ppm, whereas in the sodium dodec-2-en-1-sulfonate **10** ^{13}C spectrum it is observed at 36.9 ppm. The lack of protection suffered by carbon atoms **C8**, **C1** and **C5**, as well as the protection underwent by carbon atom **C3** in the supramolecular complexes **9** compared to coco-amido-propyl betaine **11** clearly demonstrates the existence of interactions generating supramolecular complexes **9**.

Furthermore, the lack of protection suffered by carbon atoms **C10** and **C12** and the protection underwent by carbon atoms **C11** and **C9** in the supramolecular complexes **9** compared to sodium dodec-2-en-1-sulfonate **10** confirms the presence of the same **9**.

The following main vibrational bands are observed on the supramolecular complexes **9** infrared spectrum obtained in KBr pellet: 1) an intense tension wide band at 1638 cm^{-1}, assigned to the amido carbonyl group vibration, overlapping with the sodium salt amido carbonyl group vibrational band, 2) an asymmetric intense tension wide band at 1191 cm^{-1} and a symmetric middle-intensity tension band at 1067 cm^{-1}, both assigned to the sulfonate group vibration, 3) A low-intensity flexion band at 615 cm^{-1}, assigned to the carbonyl group vibration.

4) EXPERIMENTAL EVALUATION OF THE SUPRAMOLECULAR COMPLEXES FOAMING PROPERTIES

The evaluation of the foam generation and gas piping control capacity in naturally fractured systems by the sodium alpha olefin sulfonates and alkyl amido propyl betaines interaction-derived supramolecular complexes subject matter of the present invention, was performed using three different tests: I) Foam stability measurement at atmospheric pressure conditions (Foaming test at atmospheric pressure), II) Foam stability measurement at high-pressure conditions (Foaming test at high-pressure) and III) Measurement of the capacity of the foam to control the piping of gas in naturally fractured systems at high pressure and temperature (Gas piping control test).

I) Foaming test at atmospheric pressure

The system for the generation of foam at atmospheric pressure was designed to assess the stability of foams generated by surfactants at temperatures up to 100 ºC.

The foam generation system (**Figure 1**. Scheme of the foam generation system, which allows for the foam stability to be assessed at atmospheric pressure and at

up to 100 °C) comprises the following elements: 1) gas tank (GT), 2) foam meter (FM), 3) flow-meter (F) 4) thermal bath (TB), 5) Video camera (VC), 6) Image-capturing system (ICS), 7) Flow control valve (FCV), 8) Three-way valve (TWV) and 9) Valve.

The core device of the system is the glass foam-meter, which is constituted by two concentric tubes. The outer column is 1.31 m high with a 0.0762 m diameter, and it has a 1.15 m high, 0.0508 diameter tube installed within. The outer column is charged with the solution to be evaluated (brine plus surfactant) and the spear with the sintered diffuser (which can be made out of metal or glass) is set at its center, through which the gas from the tank is injected and diffused in the surfactant-containing liquid by means of the disperser attached at its bottom end. The gas flow-regulating unit comprises three valves; a shut-off valve, a flow control valve and a three-way valve, which are connected to a flow-meter (maximum flow of 3 sfc/h) and the temperature control within the annular space is performed by means of digital circulation thermal bath.

In order to carry out the assessment of the foam stability and its foaming capacity, a procedure was developed, consisting of the following 11 steps: 1) Preparing the study solution at the concentration required by the analysis, 2) Checking the cleanness of the cell, 3) Removing the glass or steel spear from the foam generation cell, 4) Injecting 60 ml of the solution to be studied using a 20 ml glass syringe and a tube, 5) Introducing and centering the glass or steel spear, 6) Recording the liquid level initial reading, 7) Letting the gas flow for a minute at a 0.25 scf/h rate, 8) Shutting-off the gas inlet and measuring the foam's maximum height and the level of the liquid, 9) Depending on the foam disappearance rate, the time interval at which the readings must be recorded is established, 10) At each time-step, the foam height and the level of the liquid are to be read (**Figure 2.** Readings to be recorded during the foam stability test, where: TH=Total height; FH=Foam height and LH=Liquid height), 11) Determining the foam stability % at each step.

When the foam is observed to break at any point of its structure, the stop-watch is stopped and total time is recorded.

The foam stability is defined as the variation of the initial height of the foam over time (**Figure 3**. Necessary readings for the calculation of the foam stability) and it is determined according to equation 1.

$$Foam\ stability = 100 - \left(\frac{A_1(t)}{A_1(0) + A_2(0)}\right) * 100$$

Wherein:

$A_1(t)$ = *Foam height at each t time selected for measurement*

$A_1(0)$ = *Initial gas height to induce the foam*

$A_2(0)$ = *Initial foam height*

Equation 1

Example 4

Stability determination of the foam generated by sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl-betaine **11** interaction-derived supramolecular complexes **9**.

The stability of the foam generated by sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl-betaine **11** interaction-derived supramolecular complexes **9** was assessed through the Foaming test at atmospheric pressure, at a 75 ºC temperature, using a brine containing 120000 ppm, out of which 5323 ppm corresponded to divalent ions (Calcium and Magnesium), a 1% by weight concentration of supramolecular complexes **9** and nitrogen (N_2) as gas.

The established time for the attainment of each parameter (foam and liquid height) was two minutes and the minimum foam stability percentage recorded was 30%.

The stability ratio of the foam obtained with supramolecular complexes **9** over time is shown in **Figure 4** (Stability performance over time, at 1 kg/cm^2 and 75 ºC, of the foam prepared with brine at 1% by weight of supramolecular complexes **9**), and the 30% minimum stability is observed to be reached in 155 minutes.

In order to demonstrate that supramolecular complexes **9** show great advantages when used as foaming agents over the components used as raw materials for its formation, the foam stability generated by sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl betaine **11** was determined under the same experimental conditions mentioned in example **4**.

Example 5

Stability determination of the foam generated by sodium dodec-2-en-1-sulfonate **10**.

The foam stability results obtained in the foaming test at atmospheric pressure and at a 1% by weight concentration of sodium dodec-2-en-1-sulfonate **10** are shown in **Figure 5** (Stability performance over time, at 1 kg/cm^2 and 75 ºC, of the foam prepared with brine at 1% by weight of sodium dodec-2-en-1-sulfonate **10**) and the analysis of the results indicates that the minimum 30% stability is achieved in 55 minutes.

Example 6

Stability determination of the foam generated by coco-amido-propyl betaine **11.**

The foam stability results obtained in the foaming test at atmospheric pressure and at a 1% by weight concentration of coco-amido-propyl betaine **11** are shown in **Figure 6** (Stability performance over time, at 1 kg/cm^2 and 75 ºC, of the foam prepared with brine at 1% by weight of coco-amido-propyl betaine **11**) and the analysis of the results indicates that the minimum 30% stability is achieved in 35 minutes.

A comparison of the stability results obtained with foam generated by sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl betaine **11** interaction-derived supramolecular complexes **9**, sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl betaine **11** (**Figure 7**. Stability over time, at 1 kg/cm^2 and 75 ºC, of the foams generated by different chemical products (supramolecular complexes **9**, sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl betaine **11**) at 1% by weight) indicates that the foam generated by supramolecular complexes **9** is 2.8-fold more stable than the one generated by sodium dodec-2-en-1-sulfonate **10** and

4.4-fold more stable than the one generated by coco-amido-propyl betaine **11**, with these results demonstrating in a novel fashion the advantage of using the supramolecular complexes **9** derived from the interaction of sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl betaine **11** as foaming agents at atmospheric pressure, elevated temperature and high concentrations of total solids and divalent ions.

Example 7

In order to establish the effect of adding anionic surfactants on the stability of the foam generated with sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl betaine **11** interaction-derived supramolecular complexes **9**, a formulation **A** was prepared consisting of 88% by weight of supramolecular complexes **9**, 6% by weight of an anionic surfactant of the sodium 3-hydroxy-dodecil-sulfonate **15** type and 6% of coco-amido-propyl betaine **11**. The stability of formulation **A** was assessed using the foaming test at atmospheric pressure, at a temperature of 75 °C, using a brine containing 120000 ppm total solids, with 5323 corresponding to divalent ions (Calcium and Magnesium), a 1% by weight concentration of formulation **A** and nitrogen (N_2) as gas.

The foam stability results obtained in the foaming test at atmospheric pressure and at a 1% by weight concentration of formulation **A** are shown in **Figure 8** (Stability performance over time, at 1 kg/cm^2 and 75 °C, of the foam prepared with brine at 1% by weight of formulation **A**), and the analysis of the results indicates that the 30% minimum stability is reached in 140 minutes.

Example 8

In order to establish the effect of adding itaconic acid-derived oligomers on the stability of foam generated with sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl betaine **11** interaction-derived supramolecular complexes **9**, a formulation **B** was prepared, consisting of 95.2% by weight of supramolecular complexes **9** and 4.8% by weight of Poly(itaconic acid) **16** with an average molecular weight value of 1100 Dalton. The stability of formulation **B** was

evaluated by means of the foaming test at atmospheric pressure, at a temperature of 75 °C, using a brine containing 120000 ppm total solids, out of which 5323 ppm corresponded to divalent ions (Calcium and Magnesium), a 1% by weight concentration of formulation **B** and nitrogen (N_2) as gas.

The foam stability results obtained in the foaming test at atmospheric pressure and at a 1% by weight concentration of formulation **B** are shown in **Figure 9** (Stability performance over time, at 1 kg/cm^2 and 75 °C, of the foam prepared with brine at 1% by weight of formulation **B**), and the analysis of the results indicates that the 30% minimum stability is reached in 220 minutes.

Example 9

In order to establish the effect of adding partially hydrolyzed poly(acrylamide)-derived gels on the stability of foam generated with sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl betaine **11** interaction-derived supramolecular complexes **9**, a formulation **C** was prepared, consisting of 91% by weight of supramolecular complexes **9** and 9% by weight of partially hydrolyzed Poly(acrylamide) **17**. The stability of formulation **C** was evaluated by means of the foaming test at atmospheric pressure, at a temperature 75 °C, using a brine containing 120000 ppm total solids, out of which 5323 ppm corresponded to divalent ions (Calcium and Magnesium), a 1% by weight concentration of formulation **C** and nitrogen (N_2) as gas.

The foam stability results obtained in the foaming test at atmospheric pressure and at a 1% by weight concentration of formulation **C** are shown in **Figure 10** (Stability performance over time, at 1 kg/cm^2 and 75 °C, of the foam prepared with brine at 1% by weight of formulation **C**), and the analysis of the results indicates that the 30% minimum stability is reached in 600 minutes.

Example 10

In order to establish the effect of adding itaconic acid-derived oligomers and partially hydrolyzed poly(acrylamide)-derived gels on the stability of foam generated by sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl betaine

11 interaction-derived supramolecular complexes **9**, a formulation **C** was prepared, consisting of 87% by weight of supramolecular complexes **9**, 8.7% by weight of partially hydrolyzed Poly(acrylamide) **17** and 4.3% by weight of Poly(itaconic acid) **16**. The stability of formulation **D** was evaluated by means of the foaming test at atmospheric pressure, at a 75 ºC temperature, using a brine containing 120000 ppm total solids, out of which 5323 ppm corresponded to divalent ions (Calcium and Magnesium), a 1% by weight concentration of formulation **D** and nitrogen (N_2) as the gas.

The foam stability results obtained in the foaming test at atmospheric pressure and at a 1% by weight concentration of formulation **D** are shown in **Figure 11** (Stability performance over time, at 1 kg/cm^2 and 75 ºC, of the foam prepared with brine at 1% by weight of formulation **D**), and the analysis of the results indicates that the 30% minimum stability is reached in 680 minutes.

Figure 12 (Stability over time, at 1 kg/cm^2 and 75 ºC, of the foams generated by different chemical products (formulation **A**, formulation **B**, formulation **C** and formulation **D**) at 1% by weight) shows a comparison of the stability results obtained with foam generated by formulation **A**, formulation **B**, formulation **C** and formulation **D**, indicating that the foam generated by formulation **D** is 1.13-fold more stable than the one generated by formulation **C**, 3-fold more stable than the one generated by formulation **B** and 4.9-fold more stable than the one generated by formulation **A**, with these results demonstrating in a novel fashion the advantage of using itaconic acid-derived oligomers and/or partially hydrolyzed poly(acrylamide)-derived gels together with supramolecular complexes **9** as foaming agents at atmospheric pressure, high temperature and high concentrations of total solids, divalent ions and nitrogen as gas to generate the foam.

Example 11

Stability determination of the foam generated by sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl betaine **11** interaction-derived supramolecular complexes **9**, evaluated by means of the foaming test at atmospheric pressure, at a 75 ºC temperature, using a brine containing 38000 ppm total solids, out of which

6800 ppm corresponded to divalent ions (Calcium and Magnesium), a 1% by weight concentration of supramolecular complex **9** and methane (CH_4) as the gas.

The foam stability results obtained on the foaming test at atmospheric pressure and at a 1% by weight concentration of supramolecular complexes **9** are shown in **Figure 13** (Stability performance over time, at 1 kg/cm^2 and 75 °C, of the foam prepared with brine at 1% by weight of supramolecular complexes **9**), and the analysis of the results indicates that the 30% minimum stability is reached in 90 minutes.

Example 12

In order to establish the effect of adding cationic surfactants on the stability of foam generated with methane gas and sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl betaine **11** interaction-derived supramolecular complexes **9**, a formulation **E** was prepared, consisting of 91% by weight of supramolecular complexes **9** and 4.5% by weight of a cationic surfactant of the dodecyl-trimethyl-ammonium chloride **18** type and 4.5% by weight of coco-amido-propyl betaine **11**. The stability of formulation **E** was evaluated by means of the foaming test at atmospheric pressure, at a temperature of 75 °C, using a brine containing 38000 ppm total solids, out of which 6800 ppm corresponded to divalent ions (Calcium and Magnesium), a 1% by weight concentration of formulation **E** and methane (CH_4) as gas.

The foam stability results obtained on the foaming test at atmospheric pressure and at a 1% by weight concentration of formulation **E** are shown in **Figure 14** (Stability performance over time, at 1 kg/cm^2 and 75 °C, of the foam prepared with brine at 1% by weight of formulation **E**), and the analysis of the results indicates that the 30% minimum stability is reached in 93 minutes.

Example 13

In order to establish the effect of adding cationic surfactants and itaconic acid-derived oligomers on the stability of foam generated with methane gas and sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl betaine **11** interaction-derived

supramolecular complexes **9**, a formulation **F** was prepared, consisting of 87% by weight of supramolecular complex **9**, 4.4% by weight of dodecil-trimethyl-ammonium chloride **18**, 4.3% by weight of coco-amido-propyl betaine **11** and 4.3% by weight of Poly(itaconic acid) **16** with an average molecular weight value of 1100 Dalton. The stability of formulation **F** was evaluated by means of the foaming test at atmospheric pressure, at a temperature of 75 ºC, using a brine containing 38000 ppm total solids, out of which 6800 ppm corresponded to divalent ions (Calcium and Magnesium), a 1% by weight concentration of formulation **E** and methane (CH_4) as gas.

The foam stability results obtained on the foaming test at atmospheric pressure and at a 1% by weight concentration of formulation **F** are shown in **Figure 15** (Stability performance over time, at 1 kg/cm^2 and 75 ºC, of the foam prepared with brine at 1% by weight of formulation **F**), and the analysis of the results indicates that the 30% minimum stability is reached at a time of 150 minutes.

Figure 16 (Stability over time, at 1 kg/cm^2 and 75 ºC, of foams generated by different chemical products (supramolecular complexes **9**, formulation **E** and formulation **F**) at 1% by weight) shows a comparison of the stability results obtained with foam generated by dodec-2-en-1-sodium sulfonate **10** and coco-amido-propyl betaine **11** interaction-derived supramolecular complexes **9**, formulation **E** and formulation **F**, indicating that the foam generated by formulation **F** is 1.6-fold more stable than the one generated by formulation **E** and 1.7-fold more stable than the one generated by supramolecular complexes **9**, with these results demonstrating in a novel fashion the advantage of using cationic surfactants of the alkyl ammonium quaternary salts type and/or itaconic acid-derived oligomers together with supramolecular complexes **9** as foaming agents at atmospheric pressure, high temperature, high concentrations of total solids, divalent ions and nitrogen as gas to generate the foam.

Example 14

Stability determination of the foam generated by sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl betaine **11** interaction-derived supramolecular complexes **9** evaluated by means of the foaming test at atmospheric pressure, at a

temperature of 75 ºC, using a brine containing 38000 ppm total solids, out of which 6800 ppm corresponded to divalent ions (Calcium and Magnesium), a 1% by weight concentration of supramolecular complexes **9** and ethane (CH_3CH_3) as gas.

The foam stability results obtained on the foaming test at atmospheric pressure and at a 1% by weight concentration of supramolecular complex 15 are shown in **Figure 17** (Stability performance over time, at 1 kg/cm^2 and 75 ºC, of the foam prepared with brine at 1% by weight of supramolecular complexes **9**), and the analysis of the results indicates that the 30% minimum stability is reached in 77 minutes.

Example 15

In order to establish the effect of adding cationic surfactants on the stability of foam generated with ethane gas and sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl betaine **11** interaction-derived supramolecular complexes **9**, formulation **E**, consisting of 91% by weight of supramolecular complexes **9**, 4.5% by weight of a cationic surfactant of the dodecil-trimethyl-ammonium chloride **18** type and 4.5% by weight of coco-amido-propyl betaine **11**, was evaluated. The stability of formulation **E** was assessed by means of the foaming test at atmospheric pressure, at a temperature of 75 ºC, using a brine containing 38000 ppm total solids, with 6800 ppm corresponding to divalent ions (Calcium and Magnesium), a 1% by weight concentration of formulation **E** and ethane (CH_3CH_3) as gas.

The foam stability results obtained on the foaming test at atmospheric pressure and at a 1% by weight concentration of formulation **E** are shown in **Figure 18** (Stability performance over time, at 1 kg/cm^2 and 75 ºC, of the foam prepared with brine at 1% by weight of formulation **E**), and the analysis of the results indicates that the 30% minimum stability is reached in 107 minutes.

Example 16

In order to establish the effect of adding cationic surfactants and itaconic acid-derived oligomers on the stability of foam generated with ethane gas and supramolecular complexes **9** derived from the interaction of sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl betaine **11**, formulation **F**, consisting of 87% by weight of supramolecular complex **9**, 4.4% by weight of dodecil-trimethyl-ammonium chloride **18**, 4.3% by weight of coco-amido-propyl betaine **11** and 4.3% by weight of Poly(itaconic acid) **16** with an average molecular weight of 1100 Dalton, was evaluated. The stability of formulation **F** was assessed by means of the foaming test at atmospheric pressure, at a temperature of 75 ºC, using a brine containing 38000 ppm total solids, out of which 6800 ppm corresponded to divalent ions (Calcium and Magnesium), a 1% by weight concentration of formulation **F** and ethane (CH_3CH_3) as gas.

The foam stability results obtained on the foaming test at atmospheric pressure and at a 1% by weight concentration of formulation **C** are shown in **Figure 19** (Stability performance over time, at 1 kg/cm^2 and 75 ºC, of the foam prepared with brine at 1% by weight of formulation **F**), and the analysis of the results indicates that the 30% minimum stability is reached in 138 minutes.

Figure 20 (Stability over time, at 1 kg/cm^2 and 75 ºC, of foams generated by different chemical products (supramolecular complexes **9**, formulation **E** and formulation **F**) at 1% by weight) shows a comparison of the stability results obtained with foam generated by sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl betaine **11** interaction-derived supramolecular complexes **9**, formulation **E** and formulation **F**, indicating that the foam generated by formulation **F** is 1.3-fold more stable than the one generated by formulation **E** and 1.8-fold more stable than the one generated by supramolecular complexes **9**, with these results demonstrating in a novel fashion the advantage of using cationic surfactants of the alkyl ammonium quaternary salts type and/or itaconic acid-derived oligomers together with supramolecular complexes **9** as foaming agents at atmospheric pressure, elevated temperature, high concentrations of total solids, divalent ions, and ethane as gas to generate the foam.

Example 17

In order to establish the effect of a higher concentration of divalent ions in the brine employed, supramolecular complexes **9** were evaluated in a brine containing 38000 ppm total solids, out of which 6800 ppm corresponded to divalent ions (Calcium and Magnesium), at a 1% by weight concentration of supramolecular complexes **9** and using nitrogen (N_4) as gas.

The foam stability results obtained on the foaming test at atmospheric pressure and at a 1% by weight concentration of supramolecular complexes **9** are shown in **Figure 21** (Stability performance over time, at 1 kg/cm^2 and 75 ºC, of the foam prepared with brine at 1% by weight of supramolecular complexes **9**), and the analysis of the results indicates that the 30% minimum stability is reached in 25 minutes.

Example 18

In order to establish the effect of adding cationic surfactants on the stability of foam generated with sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl betaine **11** interaction-derived supramolecular complexes **9**, a formulation **G** was prepared, consisting of 50% by weight of supramolecular complexes **9**, 28% by weight of coco-amido-propyl betaine **11** and 22% by weight of a cationic surfactant of the dodecil-trimethyl-ammonium chloride **18** type. The stability of formulation **G** was evaluated by means of the foaming test at atmospheric pressure, at a temperature of 75 ºC, using a brine containing 38000 ppm total solids, out of which 6800 ppm corresponded to divalent ions (Calcium and Magnesium), a 1% by weight concentration of formulation **G** and nitrogen (N_2) as gas.

The foam stability results obtained on the foaming test at atmospheric pressure and at a 1% by weight concentration of formulation **G** are shown in **Figure 22** (Stability performance over time, at 1 kg/cm^2 and 75 ºC, of the foam prepared with brine at 1% by weight of formulation **G**), and the analysis of the results indicates that the 30% minimum stability is reached in 145 minutes.

Figure 23 (Stability over time, at 1 kg/cm^2 and 75 ºC, of foams generated by different chemical products (supramolecular complexes **9** and formulation **G**) at 1% by weight) shows a comparison of the stability results obtained with foam generated by sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl betaine **11** interaction-derived supramolecular complexes **9** and formulation **G**, indicating that the foam generated by formulation **G** is 5.8-fold more stable than the one generated by supramolecular complexes **9**, with these results demonstrating in a novel fashion the advantage of using cationic surfactants of the alkyl ammonium quaternary salts type together with supramolecular complexes **9** as foaming agents at atmospheric pressure, high temperature, high concentrations of total solids, divalent ions and nitrogen as gas to generate the foam.

II) Foam generation test at high pressure

The high-pressure foam generation system comprises a PVT cell (Pressure, temperature, volume) adapted as shown in **Figure 24** (Adapted PVT used for foam stability testing at high pressure and temperature).

The adapted PVT cell consists of a BPR valve, the purpose of which is maintaining the working pressure in the system and enabling the injection of the fluids. Within the cell and at the bottom, a disperser was adapted, through which the gas is injected; at this same part, an inlet was adapted for the injection of the brine, which has already been formulated with the foaming agent. The foam is generated within a sapphire tube, which contains a plunger that moves in order to allow for the fluids to enter; the space between the plunger and the BPR is filled with mineral oil, which enables to control the plunger's height.

In order to carry out the measurement of the stability of the foam and its foaming capability, a process was developed, comprising the following 11 steps: 1) Preparing the PVT cell (figure 24) with the corresponding adaptations for the foams test, 2) Opening the cell valves and turning on the vacuum pump for 30 minutes, 3) Injecting the gas into the cell until the pressure within the cell reaches the pressure corresponding to the pressure of the test and the height of the plunger reaches -0.327, 4) Injecting the foaming agent volume (50 cc), 4)

Recording the height of the foaming agent with respect to its reference and recording the height of the plunger with the foaming agent loaded, 5) Setting the gas cylinder at a 150 kg/cm^2 pressure, 6) Recording the difference in height between liquid and foam (if there is any), 6) Recording the starting time of the test, 7) Injecting the gas into the system through the diffuser for 5 seconds, counting with the stop-watch, 8) Cutting off the injection of gas and waiting for the gas cylinder pressure to reach 150 kg/cm^2, recording the volume of injected gas, 9) Recording the foam's initial height and starting measuring the foam and the liquid height every ten minutes, until the foam completely flattens and the foaming agent reaches the initial heights of the test, 10) Determining the foam's stability % at every time.

Example 19

Stability determination of the foam generated by sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl betaine **11** interaction-derived supramolecular complexes **9.**

The stability of the foam generated by sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl betaine **11** interaction-derived supramolecular complexes **9** was evaluated by means of the foaming test at high pressure, at a temperature of 95 ºC, a pressure of 100 kg/cm^2, using a brine containing 120000 ppm total solids, out of which 5323 ppm corresponded to divalent ions (Calcium and Magnesium), a 1% by weight concentration of supramolecular complexes **9** and nitrogen (N_2) as gas.

The time established for the attainment of each parameter (foam and liquid height) was ten minutes and the foam stability minimum percentage recorded was 45%.

Figure 25 (Stability performance over time, at 100 kg/cm^2 and 95 °C, of the foam formed with brine at 1 % by weight of supramolecular complexes **9**) shows the stability to time ratio of the foam obtained with supramolecular complex **9** and the 45% minimum stability is reached in 72 hours (4320 minutes).

A comparison between the time required on the foaming test at atmospheric pressure (example 4) and the foaming test at high pressure (example 19) for the

stability of the foam generated by supramolecular complexes **9** to increase to a 45%, indicates that the pressure increase has a positive effect on the foam stability, and that the time required to diminish the stability % of the foam on the test under high pressure conditions is 681-fold higher than the time required on the test at atmospheric pressure.

In order to demonstrate that supramolecular complexes **9** offer great advantages when used as foaming agents at high pressure over the components used as raw materials for its formation, the stability of the foam generated by sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl betaine **11** was determined under the same experimental conditions referred in example 19.

Example 20

Stability determination of the foam generated by sodium dodec-2-en-1-sulfonate **10** at high pressure.

The foam stability results obtained on the foaming test at high pressure and at a 1% by weight concentration of sodium dodec-2-en-1-sulfonate **10** are shown in **Figure 26** (Stability performance over to time, at 100 kg/cm^2 and 95 °C, of the foam generated with brine at 1 % by weight of dodec-2-en-1-sodium sulfonate **10**) and the analysis of the results indicates that the 62% minimum stability is reached in of 3.5 hours (210 minutes). After this time point the foam breaks.

Example 21

Stability determination of the foam generated by coco-amido-propyl betaine **11** at high pressure.

The foam stability results obtained on the foaming test at high pressure and at a 1% by weight concentration of coco-amido-propyl betaine **11** are shown in **Figure 27** (Stability performance over time, at 100 kg/cm^2 and 95 °C, of the foam formed with brine at 1 % by weight of coco-amido-propyl betaine **11**) and the analysis of

the results indicates that the 50% minimum stability is reached in 2.1 hours (126 minutes). After this time point the foam breaks.

A comparison of the stability results obtained with foam generated by sodium dodec-2-en-1- sulfonate **10** and coco-amido-propyl betaine **11** interaction-derived supramolecular complexes **9**, sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl betaine **11** on the high-pressure test (**Figure 28**. Stability over time, at 100 kg/cm^2 and 95 °C, of the foams generated by different chemical products (supramolecular complexes **9**, sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl betaine **11**) at 1% by weight) indicates that the foam generated by supramolecular complexes **9** is 6.5-fold more stable than the one generated by sodium dodec-2-en-1-sulfonate **10** and 18-fold more stable than that generated by coco-amido-propyl betaine **11**, with these results demonstrating in a novel fashion the advantage of using sodium dodec-2-en-1 sulfonate **10** and coco-amido-propyl betaine **11** interaction-derived supramolecular complexes **9** as foaming agents at high pressure, elevated temperature and high total solid and divalent ions concentration.

III) Gas piping control test

The experimental array developed to assess the capacity of the foam that will control the piping of gas in fractured systems is shown in **Figure 29** (Experimental array used for the control of gas piping).

The experimental procedure to assess the capacity of the foam that will control the piping of gas in fractured systems comprises the following 4 steps:

1. Preparation of the artificial fracture system.

An artificial fractures system is built, consisting of 4 low-permeability stoppers longitudinally cut in the middle, serially attached in order to form a composite medium with an artificial fracture (**Figure 30**. Artificial longitudinal fracture used for the gas piping control test). This system is placed on the core-holder and installed in the experimental array shown in **Figure 31**. Once installed, its

permeability (40 mD) and its porosity (3.67%) are experimentally determined. An overcharge pressure is applied (300 psi higher than the displacement pressure) using the BC3 pump. Then, the system is saturated with the formation's synthetic brine and it is brought to irreducible water conditions with oil. The system is left to age for two weeks under reservoir pressure and temperature conditions.

2. Foam formation.

At this step, three cylinders are used: one containing nitrogen (B1), another containing brine (B2) dosed as the foaming agent, and the cylinder receiving the formed foam (B3).

The gas (BC1 pump) and brine (BC2 pump) injection is carried out simultaneously; the outputs used for each one of these fluids' injection depend on the desired amount of foam. The liquids are mixed in a system formed by two concentric tubes and the mixed liquids are passed through a high porosity and permeability packed column (PC) in order to ensure the mixing. At the end of the packed column, a capillary glass tube is attached to visually ensure that the foam is formed. The foam generated is collected in the third cylinder (B3); if required, the foam generated can be returned to the gas cylinder.

3. Foam injection.

The foam is injected into the fractured medium using the BC1 pump, attaching a capillary glass tube (TC1) before the fractured system in order to visually check the foam generated. At the end of the fractured system there is also a visual cell (TC2) to identify the foam's stability once it has passed through the fracture system. Before and after the fractured system there are two pressure transductors.

4. Gas advance control.

In order to test the blocking capacity of the fracture with the foam, gas is injected counter flow-wise using the BC2 pump, maintaining a 10 psi pressure differential (the pressure at the other end is the reservoir pressure), leaving the system stand for two weeks (Figure 29).

Example 22

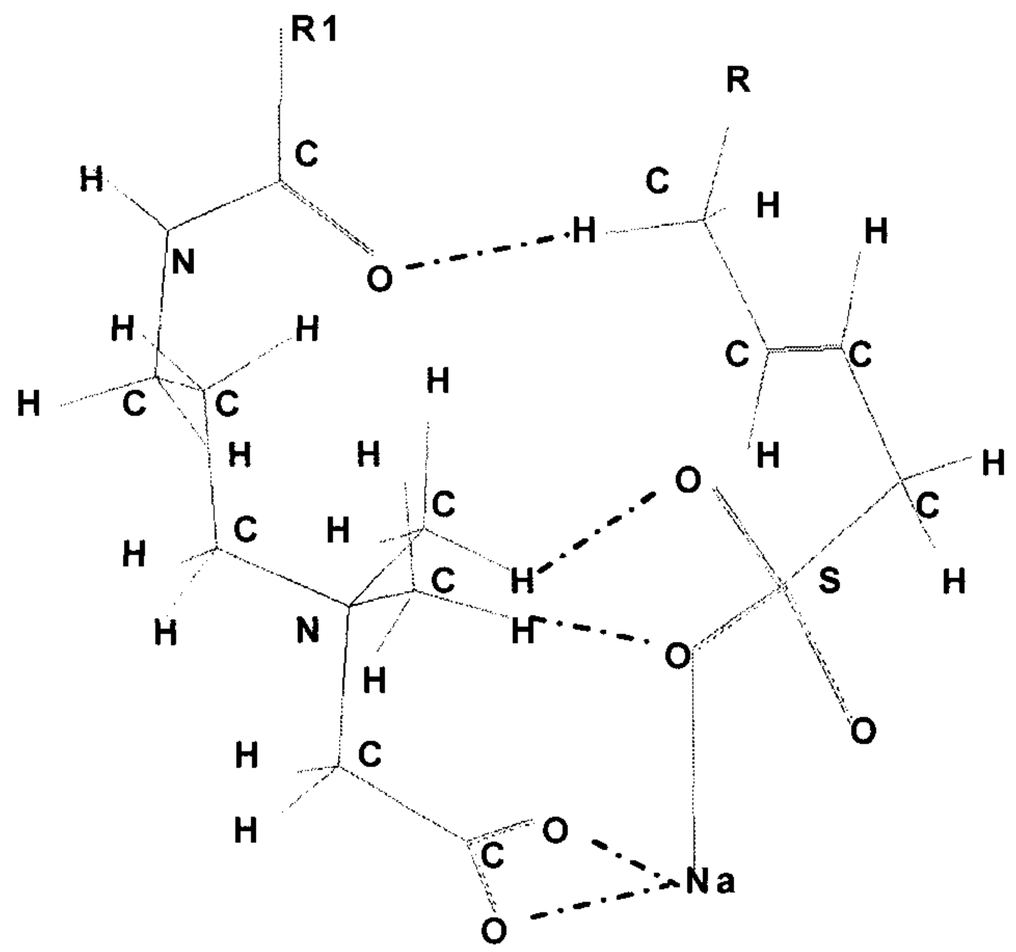
Stability determination of the foam generated by sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl betaine **11** interaction-derived supramolecular complexes **9**.

The capacity of the foam generated by sodium dodec-2-en-1-sulfonate **10** and coco-amido-propyl betaine **11** interaction-derived supramolecular complexes **9** to control the piping of gas in fractured systems at high pressure and temperature was evaluated using the gas piping control test, at a temperature of 95 °C, a pressure of 100 kg/cm^2, using a brine containing 120000 ppm total solids, with 5323 ppm of them corresponding to divalent ions (Calcium and Magnesium), a 1% by weight concentration of supramolecular complexes **9** and nitrogen (N2) as gas. The counter flow gas pressure was such, that it allowed reaching a 10 psi pressure difference and the system was left to stay for two weeks.

The pressure differential remained stable throughout the two weeks, thus demonstrating that the foam is efficiently controlling the gas piping problems in fractured systems under high temperature, pressure and salinity conditions.

What is claimed is:

1. A composition with foaming properties containing as active component, in a % by weight ranging from 0.5 to 99.5% supramolecular complexes comprising a mixture of sodium alpha olefin sulfonates and alkyl amido propyl betaines in a relation by weight from 1:1 to 1:2, according to the following structural formula:



wherein R and R1 are linear or branched independent alkyl chains and with a length thereof ranging from 1 to 30 carbon atoms.

2. A composition with foaming properties according to claim 1, wherein the supramolecular complexes comprise a mixture of sodium alpha olefin sulfonates and alkyl amido propyl betaines.

3. A composition with foaming properties according to claim 1, wherein said sodium alpha olefin sulfonates are selected from the group consisting of sodium but-2-en-1-sulfonate, sodium pent-2-en-1-sulfonate, sodium hex-2-en-1-sulfonate, sodium hept-2-en-1-sulfonate, sodium oct-2-en-

1-sulfonate, sodium non-2-en-1-sulfonate, sodium dec-2-en-1-sulfonate, sodium undec-2-en-1-sulfonate, sodium dodec-2-en-1-sulfonate, sodium tetradec-2-en-1-sulfonate, sodium hexadec-2-en-1-sulfonate and the mixture of one or more of said sodium alpha olefin sulfonates.

4. A composition with foaming properties according to claim 1, wherein said alkyl amido propyl betaines-based compounds are selected from the group consisting of ethyl-amido-propyl-betaine, propyl-amido-propyl-betaine, butyl-amido-propyl-betaine, pentyl-amido-propyl-betaine, hexyl-amido-propyl-betaine, heptyl-amido-propyl-betaine, octyl-amido-propyl-betaine, nonyl-amido-propyl-betaine, decyl-amido-propyl-betaine, undecyl-amido-propyl-betaine, coco-amido-propyl-betaine, and mixtures of one or more of said alkyl amido propyl betaines.

5. A composition with foaming properties according to claim 1, wherein said composition further comprises aqueous solvents, alcohols or a mixture of aqueous solvents and alcohols.

6. A composition with foaming properties according to claim 1, further comprising an aqueous solvent or alcohol or mixture of aqueous solvents and alcohols % by weight ranges from 0.5 to 99.5%.

7. A composition according to claim 1, comprising said active component in an amount of 10 to 90% by weight.

8. A composition according to claim 1, wherein said composition is a foam obtained by mixing with a gas selected from the group consisting of nitrogen, oxygen, carbon dioxide, natural gas, methane, propane, butane, and mixtures of two or more of said gases.

9. A composition according to claim 1, further comprising a sodium 3-hydroxy-alkyl-sulfonate anionic surfactant.

10. A composition according to claim 1, further comprising an alkyl ammonium quaternary salt cationic surfactant.

11. A composition according to claim 10, wherein the cationic surfactant is an alkyl trimethyl ammonium bromide or chloride.

12. A composition according to claim 10, wherein the sodium alpha olefin sulfonates, alkyl amido propyl betaines and alkyl ammonium quaternary salt are present in a weight ratio of 1:2:1 to 1:1.01:0.01.

13. A composition according to claim 1, further comprising a divalent ion sequestrant.

14. A composition according to claim 13, wherein said divalent ion sequestrant is an itaconic acid-derived oligomer or copolymer having an average molecular weight ranging from 200 to 20000 Dalton.

15. A composition according to claim 13, wherein the sodium alpha olefin sulfonates, alkyl amido propyl betaines and divalent ion sequestrant are present in a weight ratio of 1:1:0.5 to 1:1:0.01.

16. A composition according to claim 1, further comprising an alkyl ammonium quaternary salt and a divalent ion sequestrant.

17. A composition according to claim 16, wherein the sodium alpha olefin sulfonates, alkyl amido propyl betaines, cationic surfactant and divalent ion sequestrant are present in a weight ratio of 1:2:1:0.5 to 1:1.01:0.01.

18. A composition according to claim 1, further comprising a gel.

19. A composition according to claim 18, wherein the gel is a polymer or copolymer selected from the group consisting of a polyacrylamide, a partially hydrolyzed polyacrylamide, xanthan gum, poly(itaconic acid), poly(acrylic acid), poly(itaconic acid-co-acrylic acid), a poly(itaconate) and a poly(acrylate).

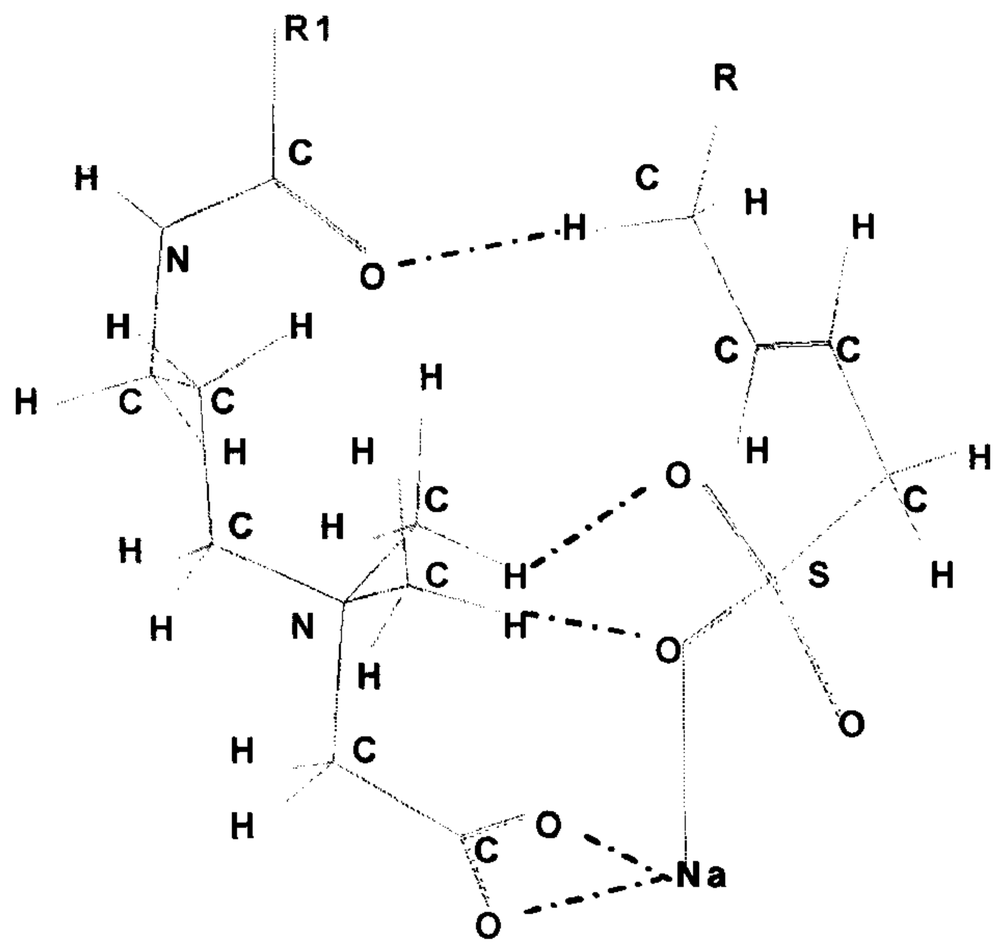
20. A composition according to claim 18, wherein the gel is selected from the group consisting of partially hydrolyzed polyacrylamide and xanthan gum.

21. A composition according to claim 18, wherein the sodium alpha olefin sulfonates, alkyl amido propyl betaines and gel are present in a weight ratio of 1:1:0.2 to 1:1:0.01.

22. A composition according to claim 1, further comprising anionic surfactants.

23. A process for enhancing recovery and production from a gas or oil well, said process comprising the steps of:

1) preparing a foam from brine, a gas and a foaming composition containing as active component, in a % by weight ranging from 0.5 to 99.5% supramolecular complexes comprising a mixture of sodium alpha olefin sulfonates and alkyl amido propyl betaines in a relation by weight from 1:1 to 1:2, according to the following structural formula:



wherein R and R1 are independently a linear or branched alkyl having 1-30 carbon atoms;

2) injecting the foam into the well;

3) pumping foam from the well into a fractured reservoir;

4) controlling gas advance within the fractured reservoir through the injected foam.

24. The process of claim 23, wherein said foam further comprises an alkyl quaternary ammonium salt cationic surfactant.

25. The process of claim 23, wherein said foam further comprises a sodium 3-hydroxy-alkyl-sulfonate anionic surfactant.

26. The process of claim 23, wherein said foam further comprises an alkyl quaternary ammonium salt cationic surfactant and divalent ions sequestrants.

27. The process of claim 23, wherein said foam further comprises an alkyl quaternary ammonium salt cationic surfactant, a divalent ion sequestrant and a gel.

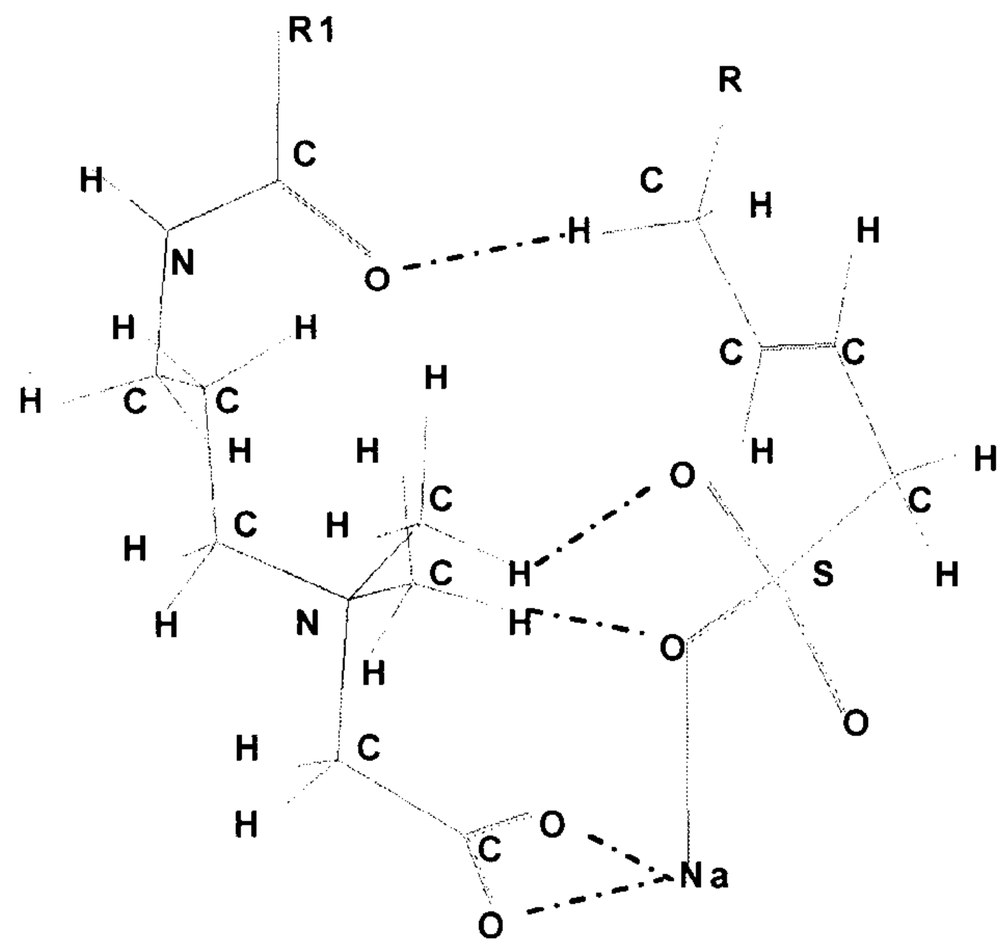
28. The process of claim 23, wherein said well is formed in a naturally fractured carbonate,

29. The process of claim 23, wherein said foam is injected into a production well.

30. The process of claim 23, wherein said foam is continuously supplied to an injector well.

31. A composition with foaming properties containing as active component, in a % by weight ranging from 0.5 to 99.5%:

(a) supramolecular complexes comprising a mixture of sodium alpha olefin sulfonates and alkyl amido propyl betaines in a relation by weight from 1:1 to 1:2, according to the following structural formula:



wherein R and R1 are linear or branched independent alkyl chains and with a length thereof ranging from 1 to 30 carbon atoms, and

(b) sodium hydroxyl alkyl sulfonates,

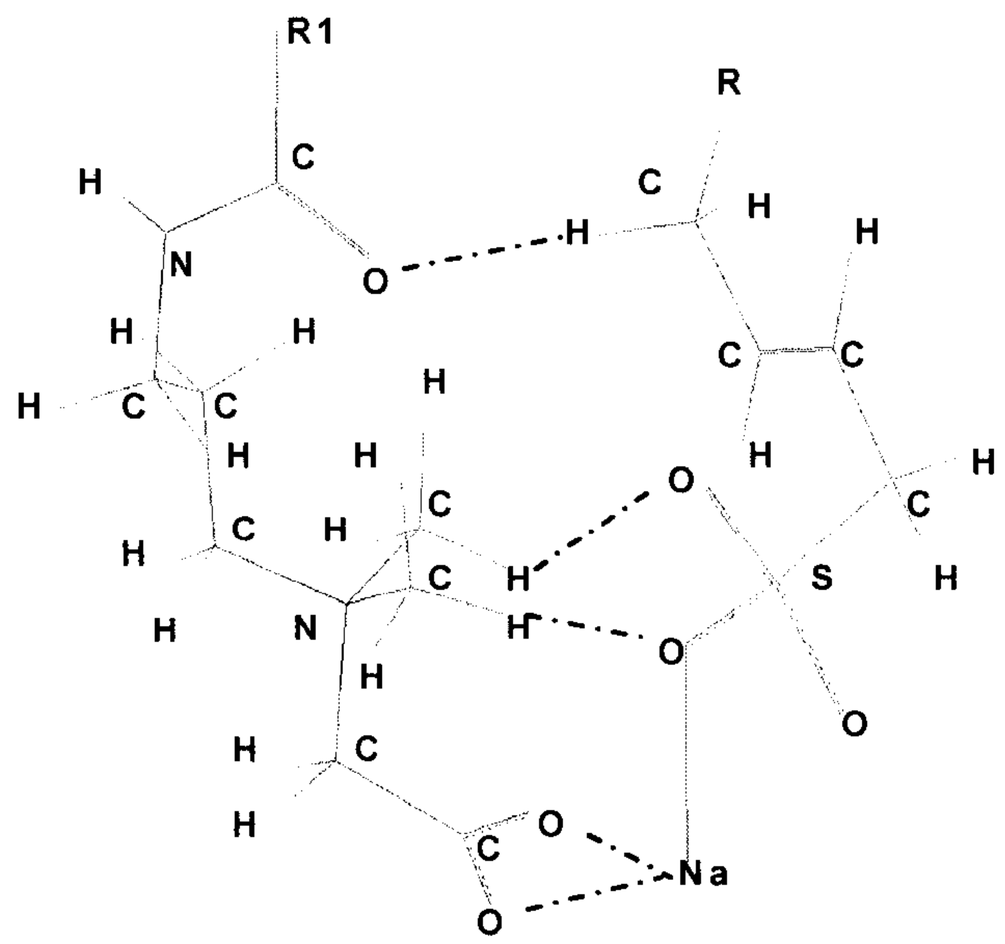
(c) alkyl ammonium quaternary salts, and

(d) divalent ions sequestrants,

where components (a), (b), (c) and (d) are present in a weight ratio of 2.01:0.67:0.01:0.01 to 3:0.75:1:0.5; respectively in said active component.

32. A composition with foaming properties containing as active component, in a % by weight ranging from 0.5 to 99.5%:

(a) supramolecular complexes comprising a mixture of sodium alpha olefin sulfonates and alkyl amido propyl betaines in a relation by weight from 1:1 to 1:2, according to the following structural formula:



wherein R and R1 are linear or branched independent alkyl chains and with a length thereof ranging from 1 to 30 carbon atoms, and

(b) sodium hydroxyl alkyl sulfonates,

(c) alkyl ammonium quaternary salts, and

(d) a gel,

where components (a), (b), (c) and (d) are present in a weight ratio of 2:0.5:0.01 to 2:0.5:0.2; respectively in said active component.

33. A process of claim 23 where the foaming composition is the composition defined in claim 31.

34. A process of claim 23 where the foaming composition is the composition defined in claim 32.

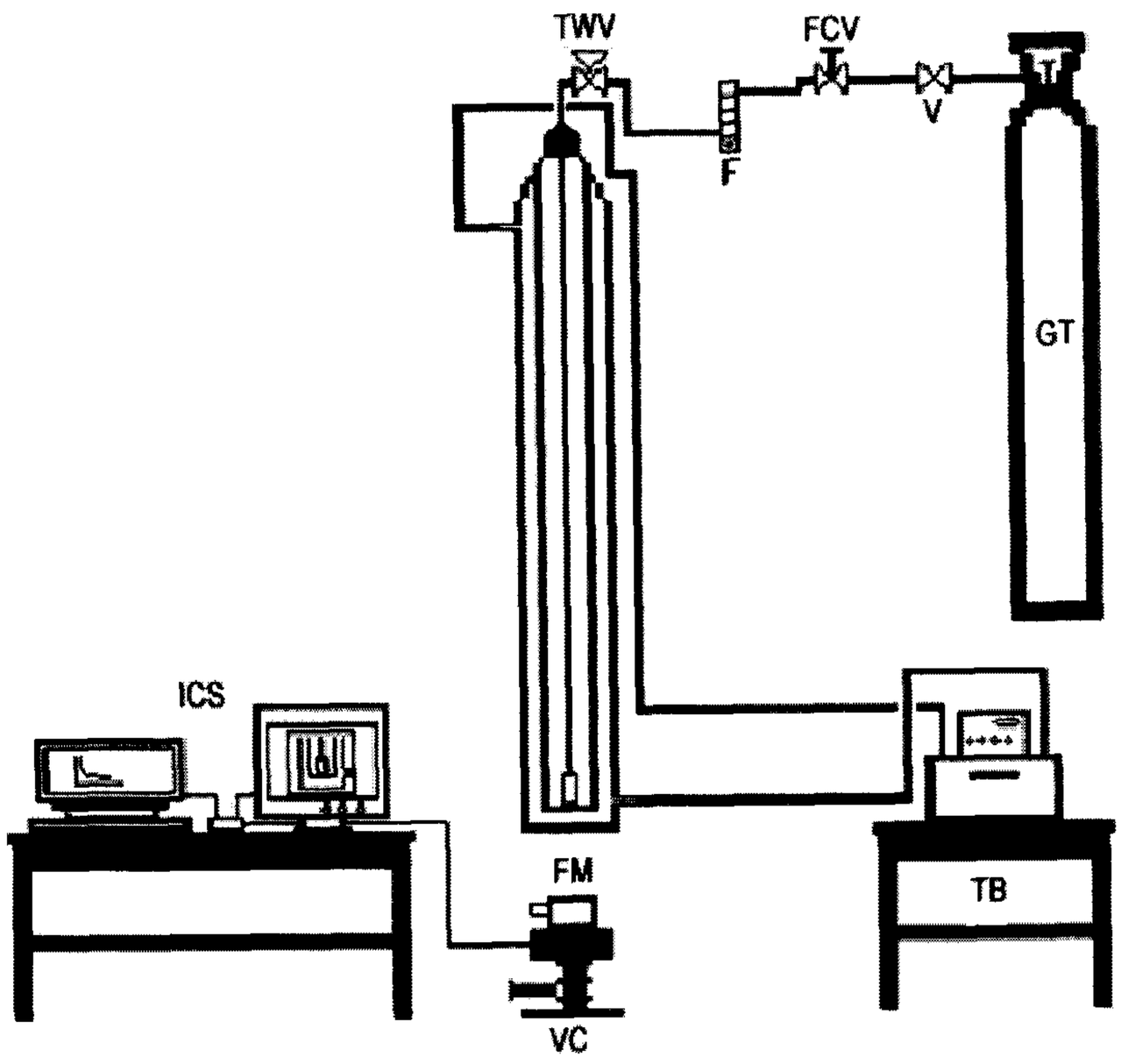


Figure 1

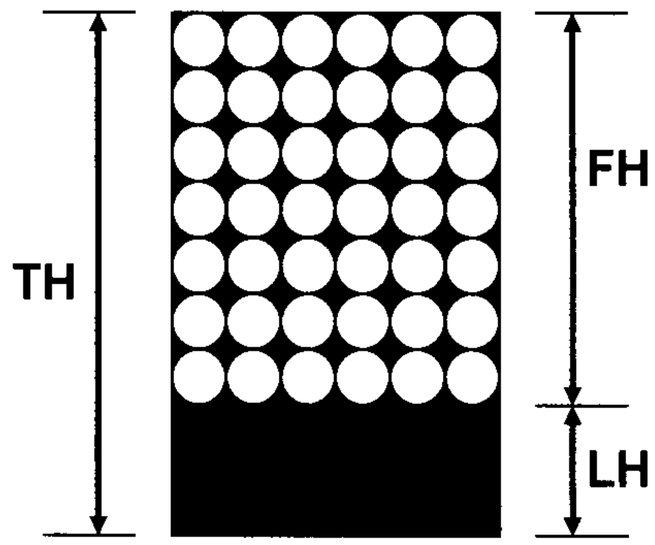


Figure 2

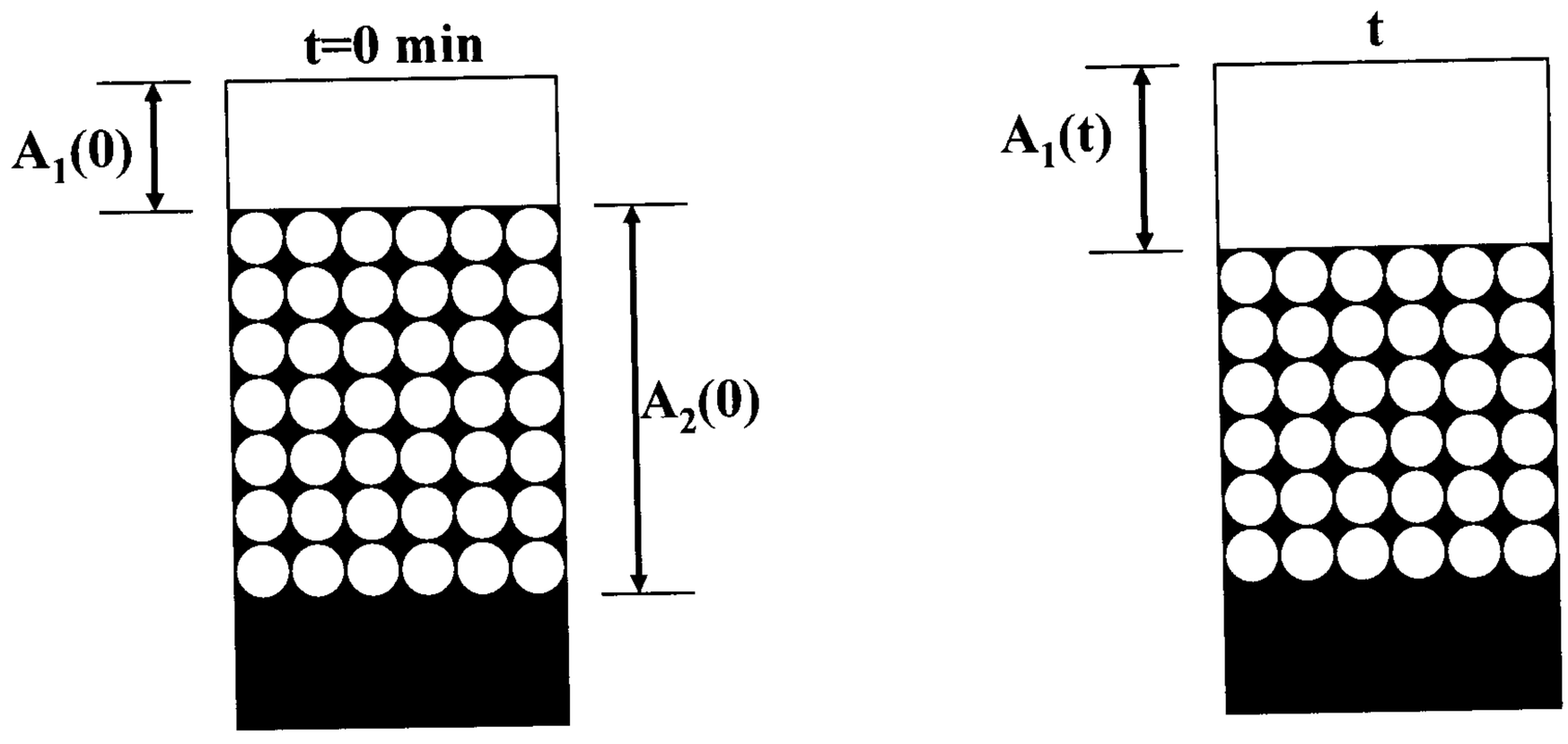


Figure 3

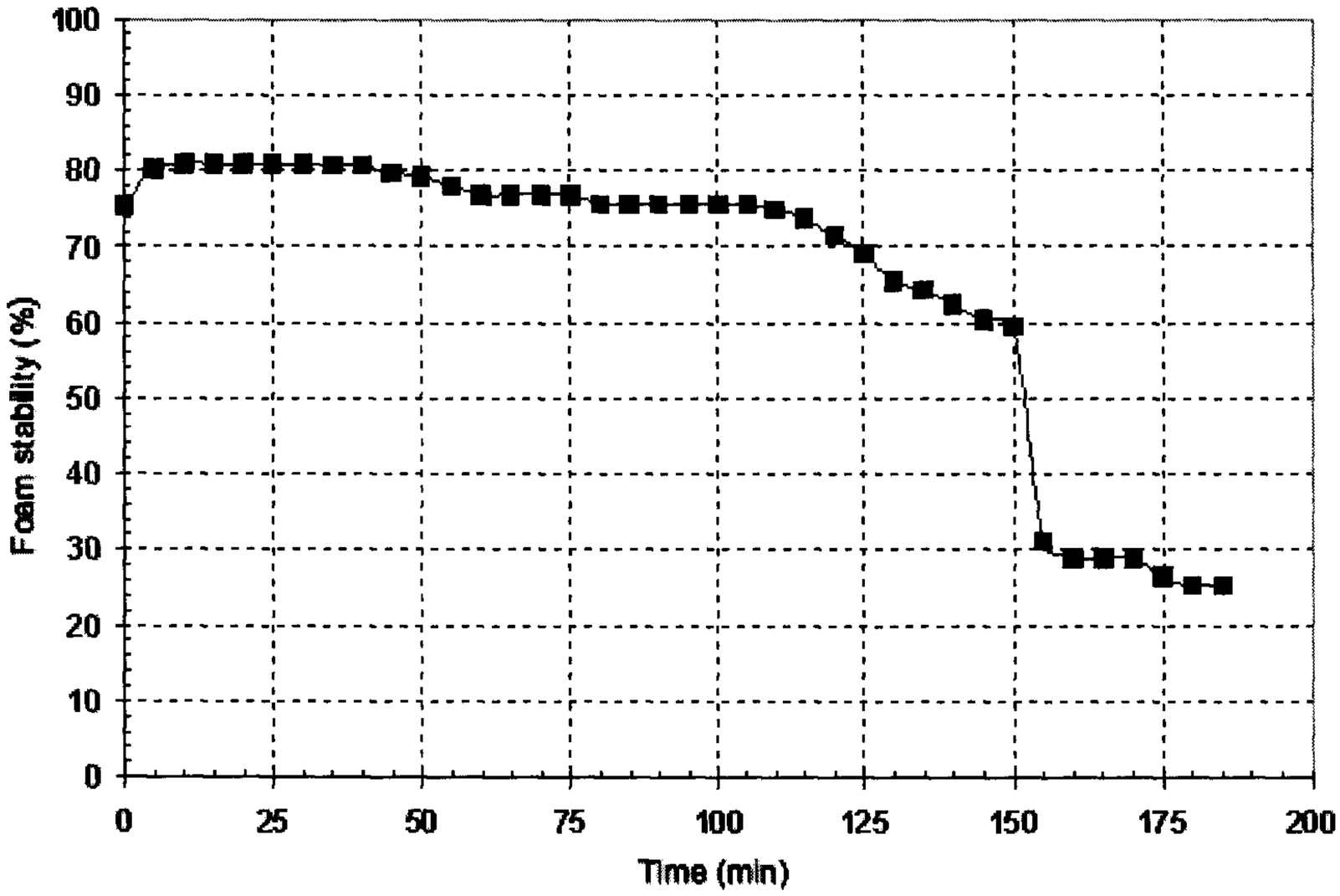

Foam stability (%)
Time (min)
0
10
20
30
40
50
60
70
80
90
100
0
25
50
75
100
125
150
175
200

Figure 4

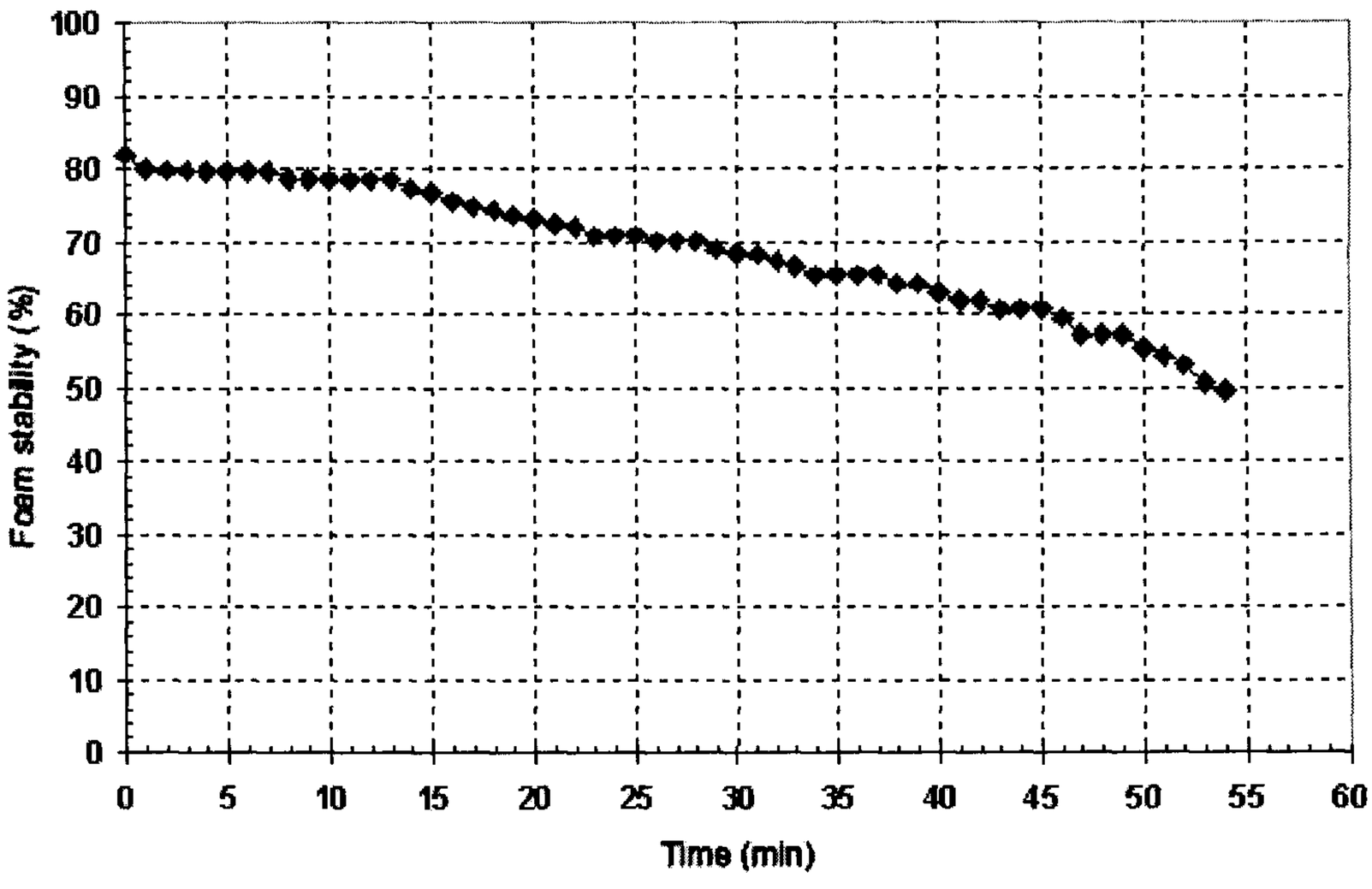

100
90
80
70
60
50
40
30
20
10
0
Foam stability (%)
0
5
10
15
20
25
30
35
40
45
50
55
60
Time (min)

Figure 5

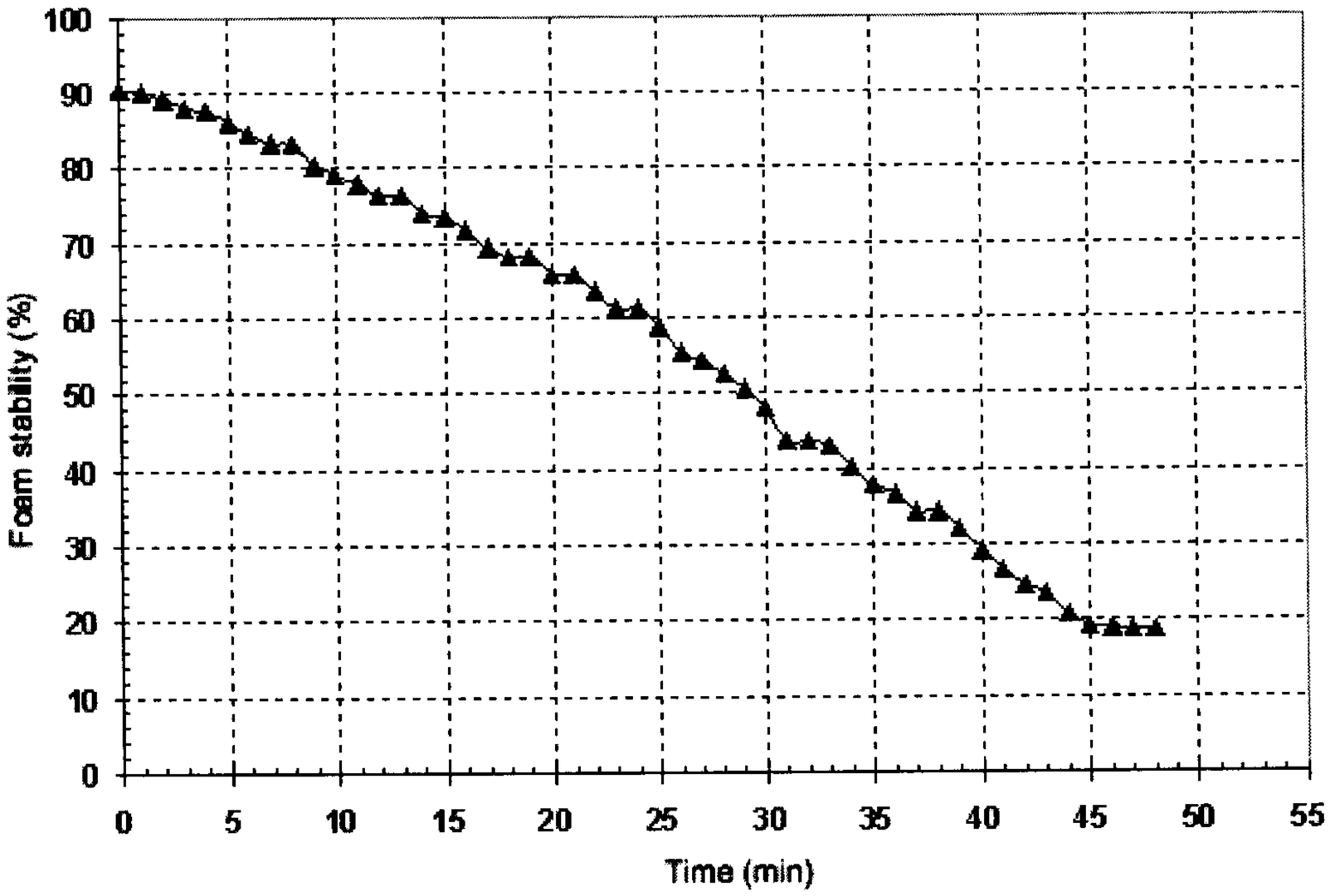

Foam stability (%)
100
90
80
70
60
50
40
30
20
10
0
0
5
10
15
20
25
30
35
40
45
50
55
Time (min)

Figure 6

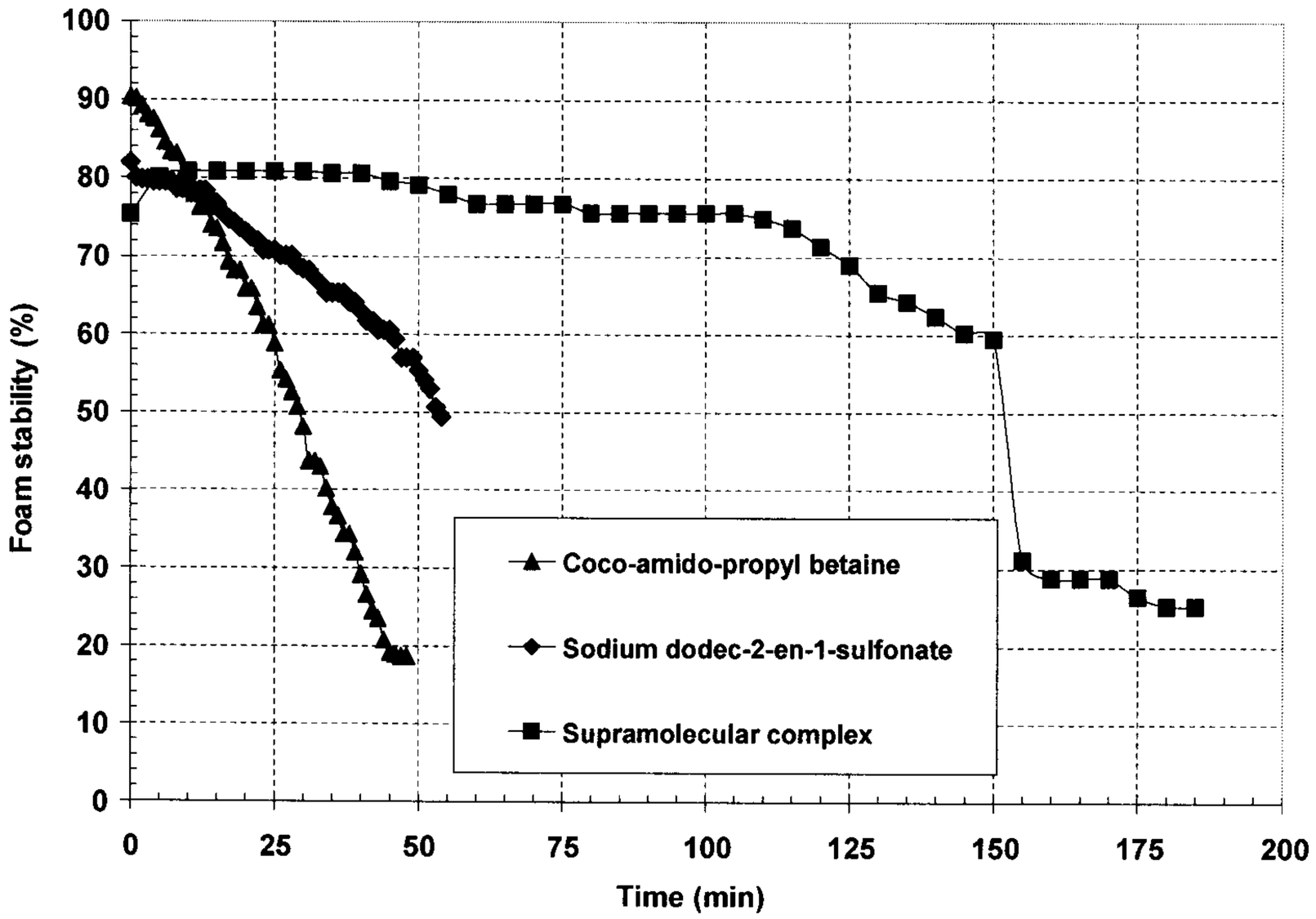

Foam stability (%)
Time (min)
0
10
20
30
40
50
60
70
80
90
100
0
25
50
75
100
125
150
175
200
Coco-amido-propyl betaine
Sodium dodec-2-en-1-sulfonate
Supramolecular complex

Figure 7

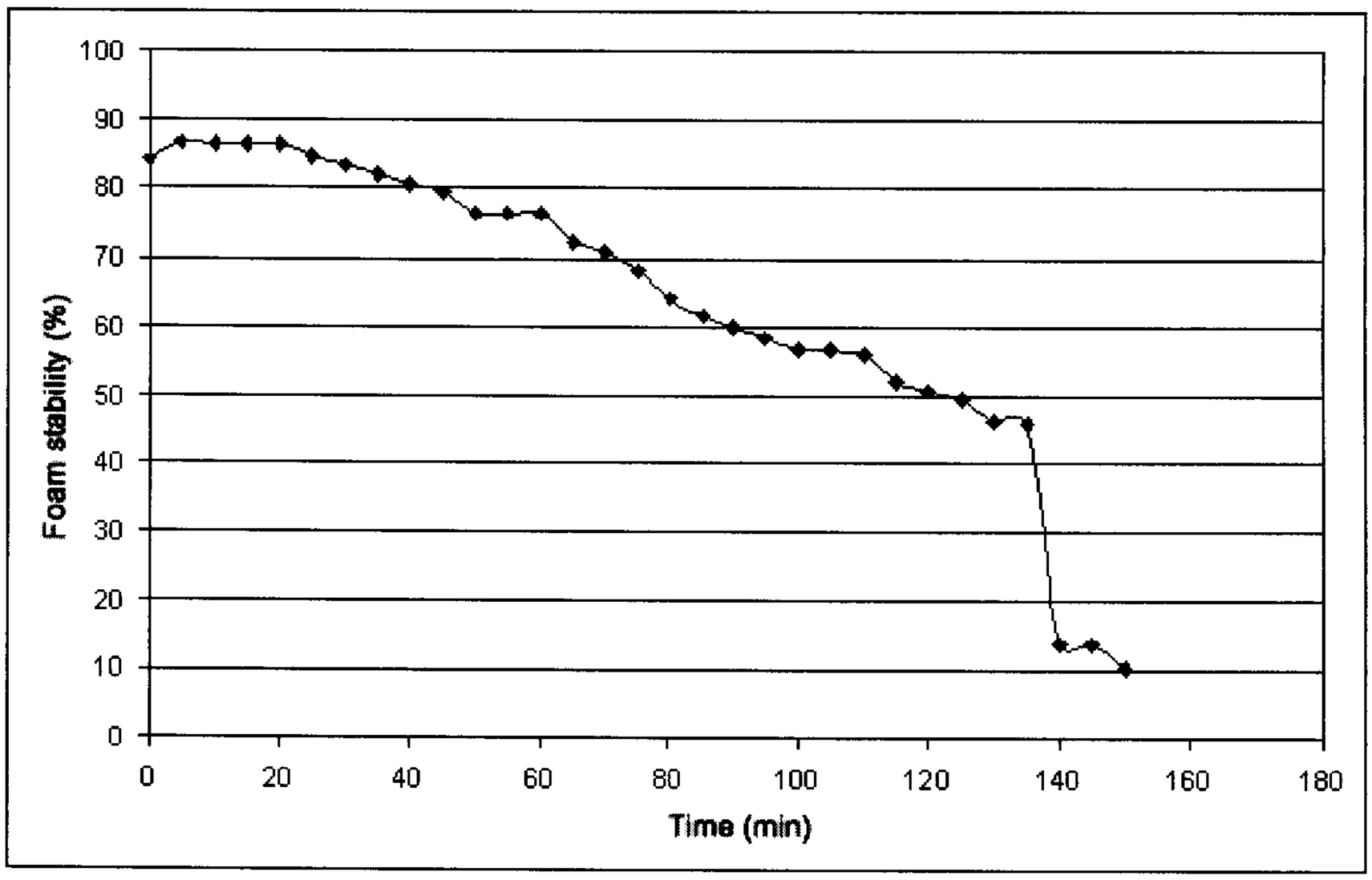

100
90
80
70
60
50
40
30
20
10
0
Foam stability (%)
0
20
40
60
80
100
120
140
160
180
Time (min)

Figure 8

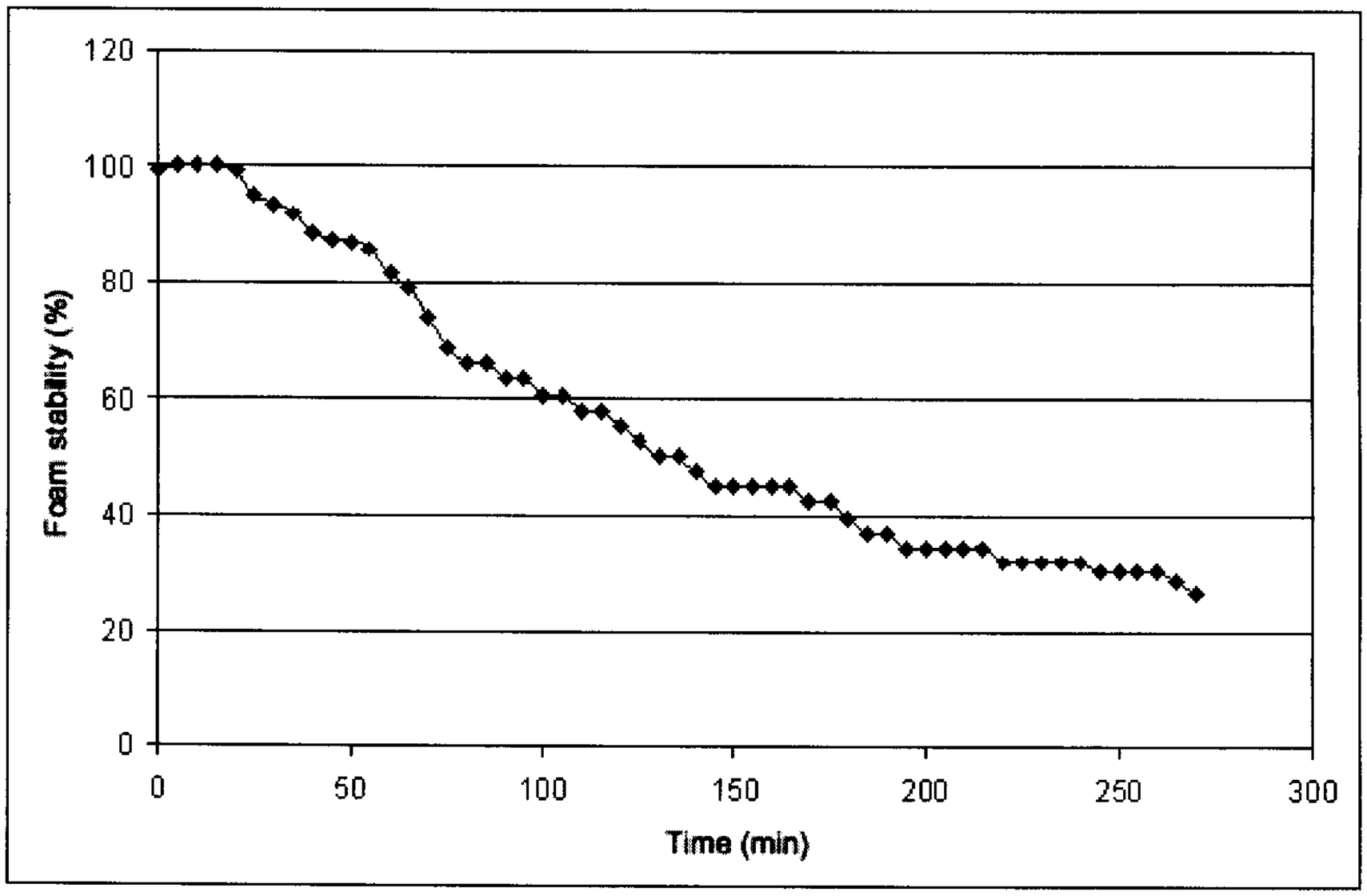

120
100
80
60
40
20
0
Foam stability (%)
0
50
100
150
200
250
300
Time (min)

Figure 9

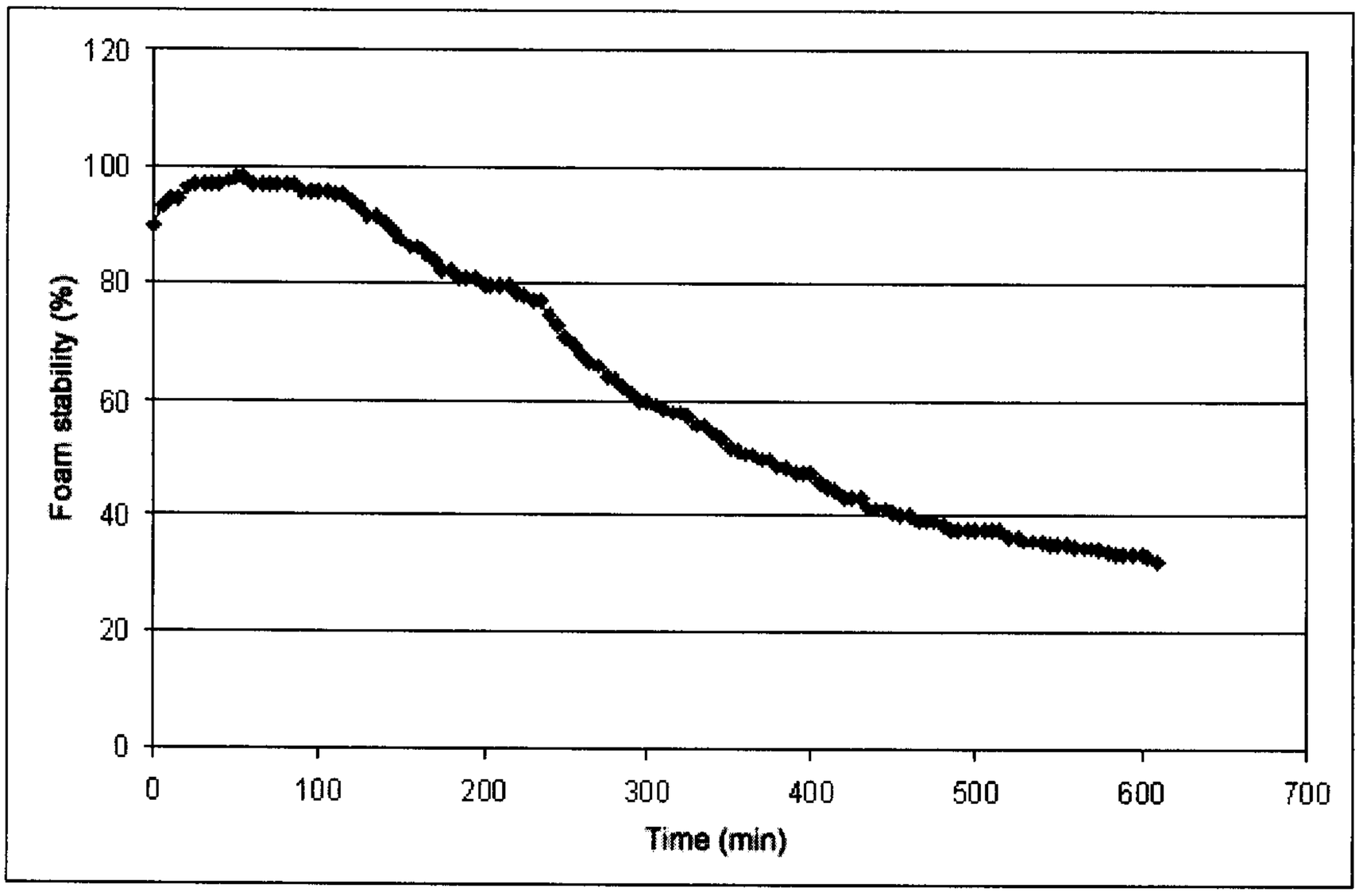

120
100
80
60
40
20
0
Foam stability (%)
0
100
200
300
400
500
600
700
Time (min)

Figure 10

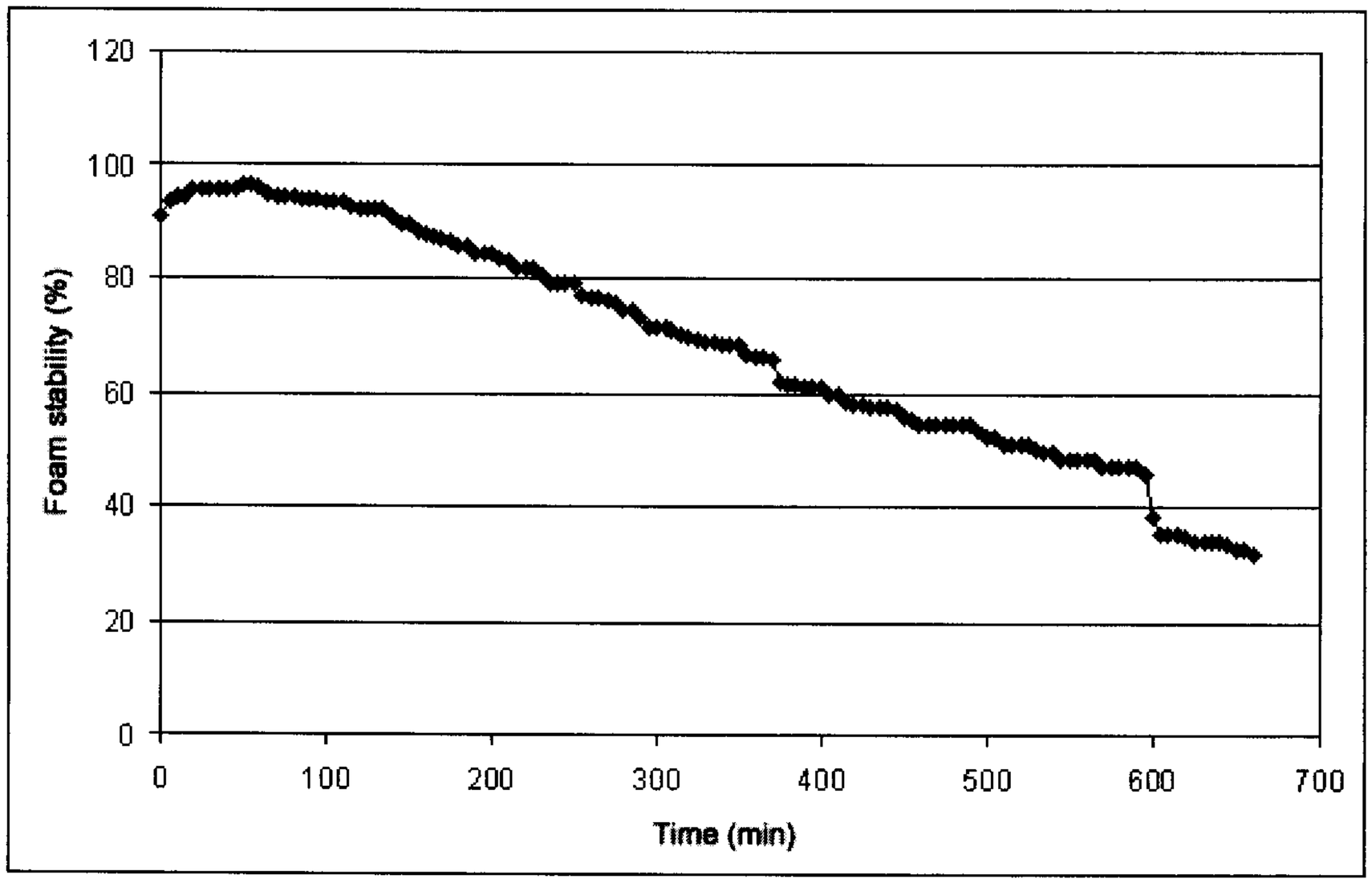

120
100
80
60
40
20
0
Foam stability (%)
0
100
200
300
400
500
600
700
Time (min)

Figure 11

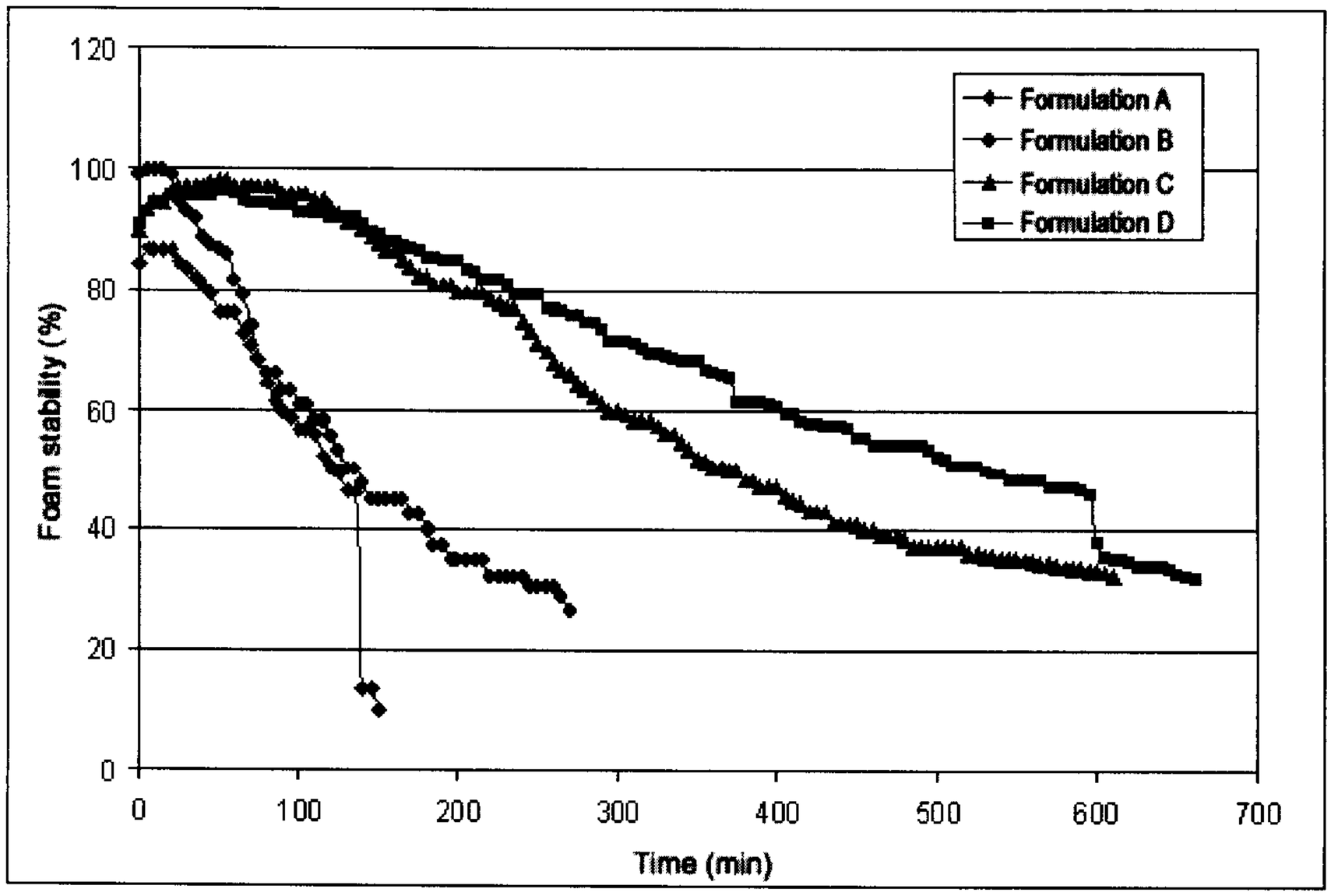

120
100
80
60
40
20
0
Foam stability (%)
0
100
200
300
400
500
600
700
Time (min)
Formulation A
Formulation B
Formulation C
Formulation D

Figure 12

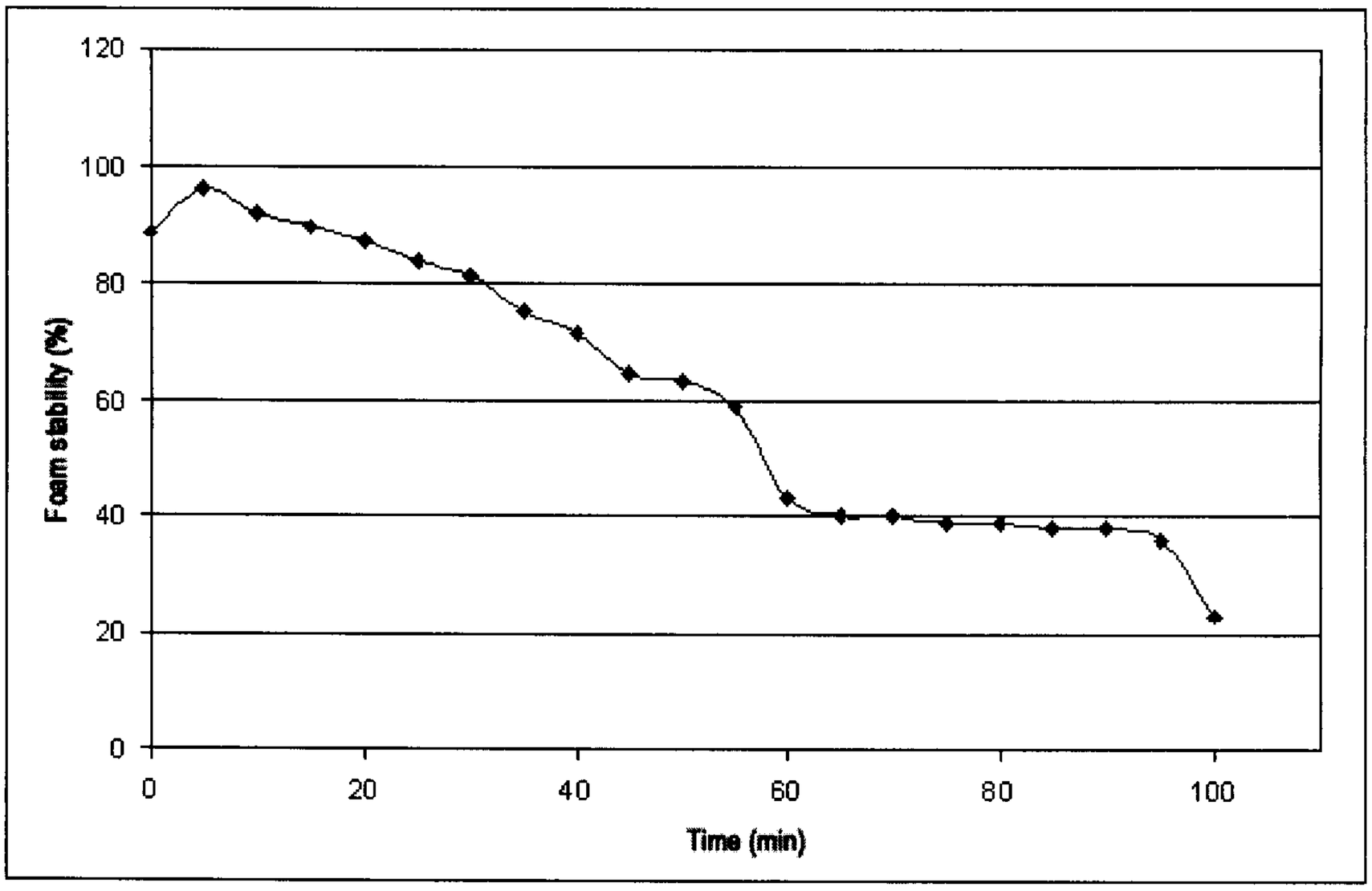


Figure 13

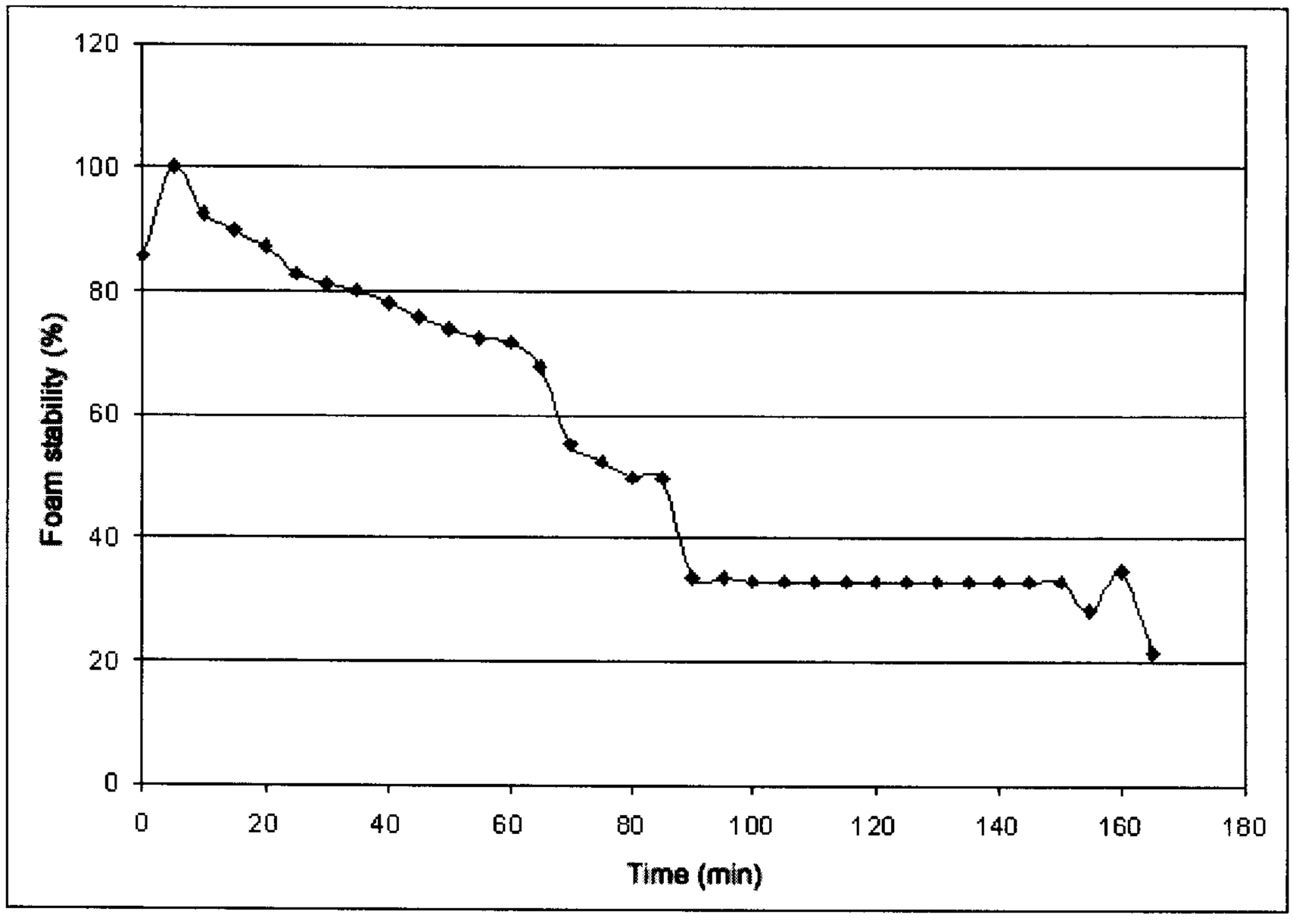

120
100
80
60
40
20
0
Foam stability (%)
0
20
40
60
80
100
120
140
160
180
Time (min)

Figure 14

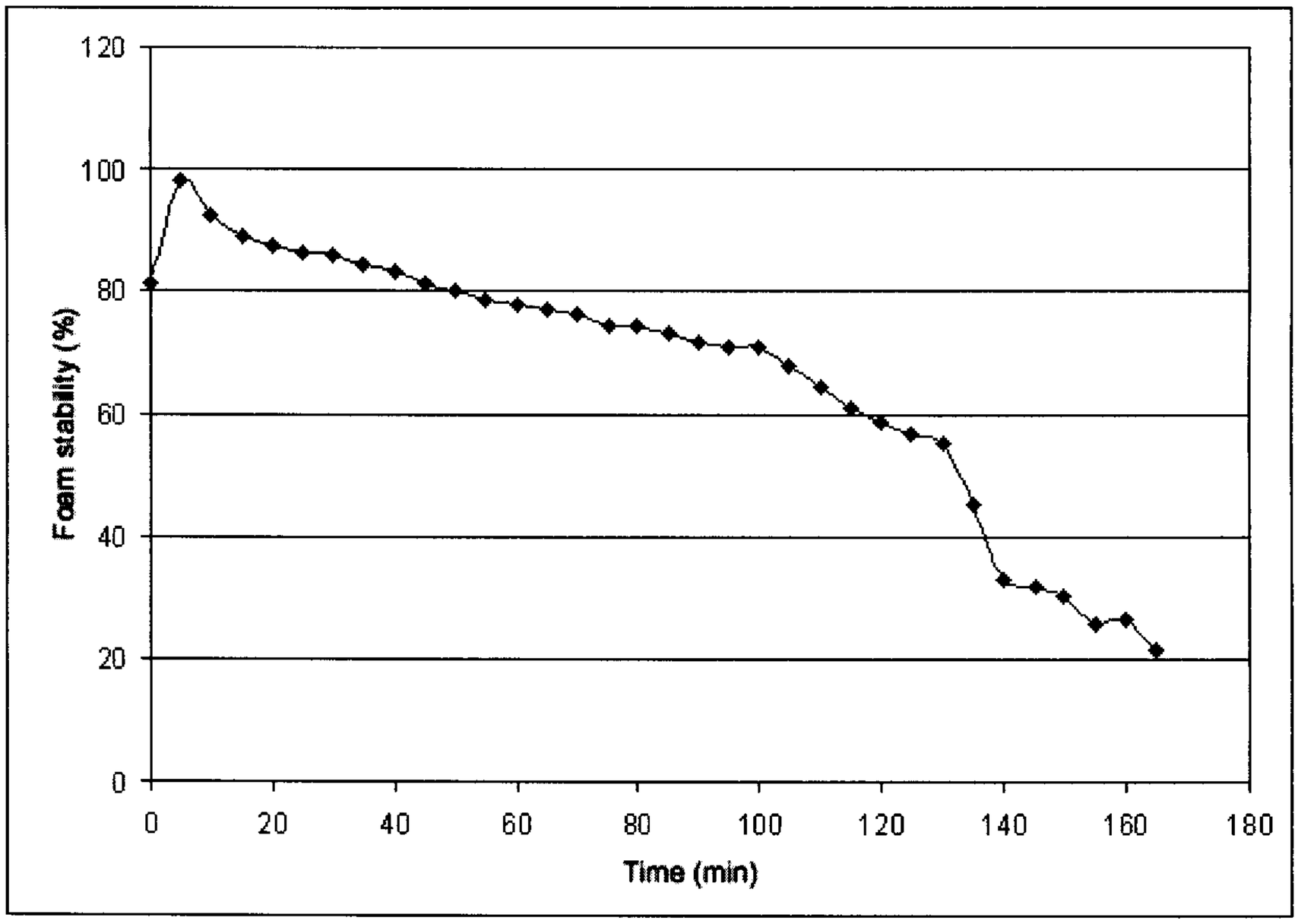

120
100
80
60
40
20
0
Foam stability (%)
0
20
40
60
80
100
120
140
160
180
Time (min)

Figure 15

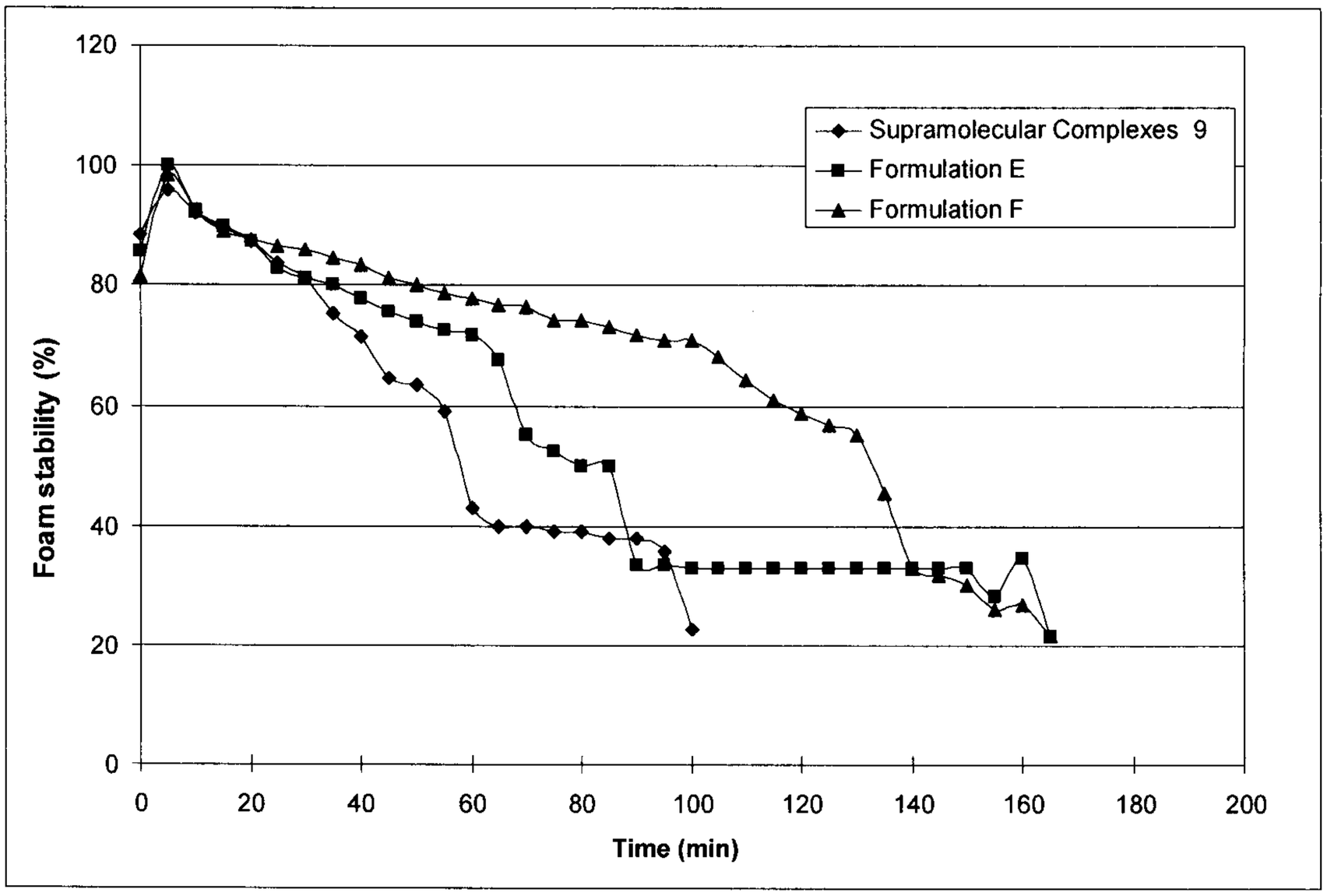

120
100
80
60
40
20
0
Foam stability (%)
0
20
40
60
80
100
120
140
160
180
200
Time (min)
Supramolecular Complexes 9
Formulation E
Formulation F

Figure 16

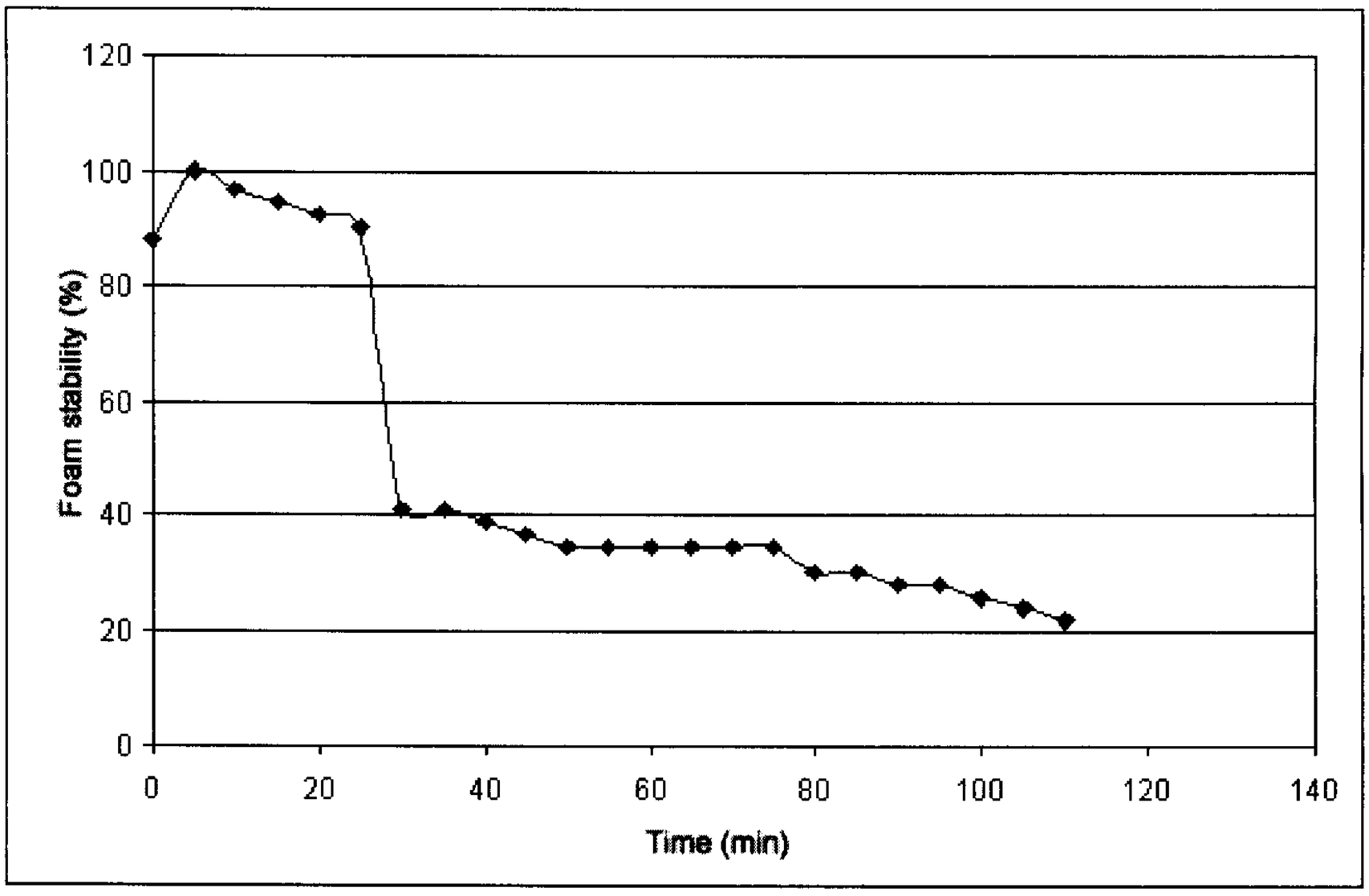

120
100
80
60
40
20
0
Foam stability (%)
0
20
40
60
80
100
120
140
Time (min)

Figure 17

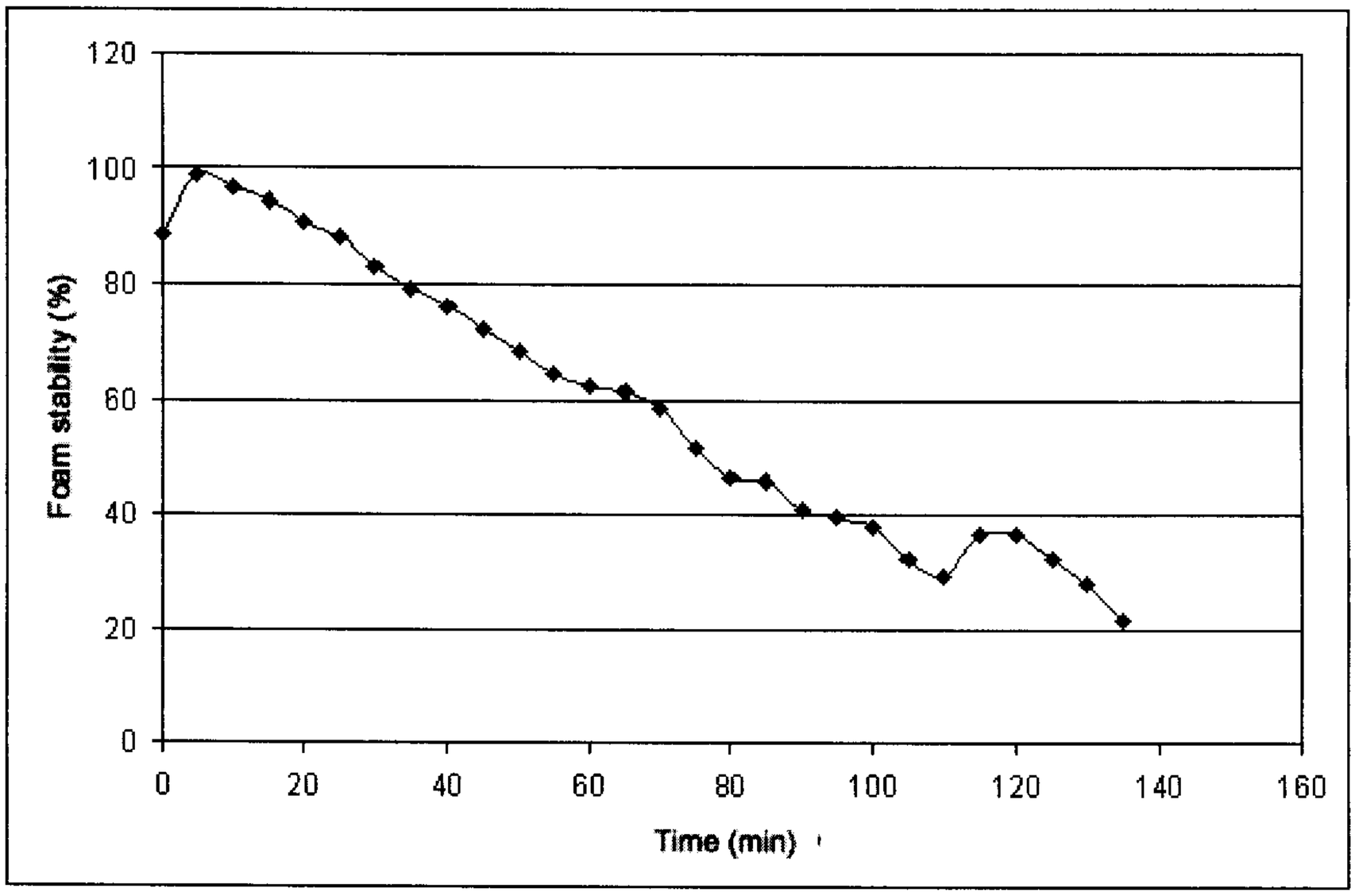

120
100
80
60
40
20
0
Foam stability (%)
0
20
40
60
80
100
120
140
160
Time (min)

Figure 18

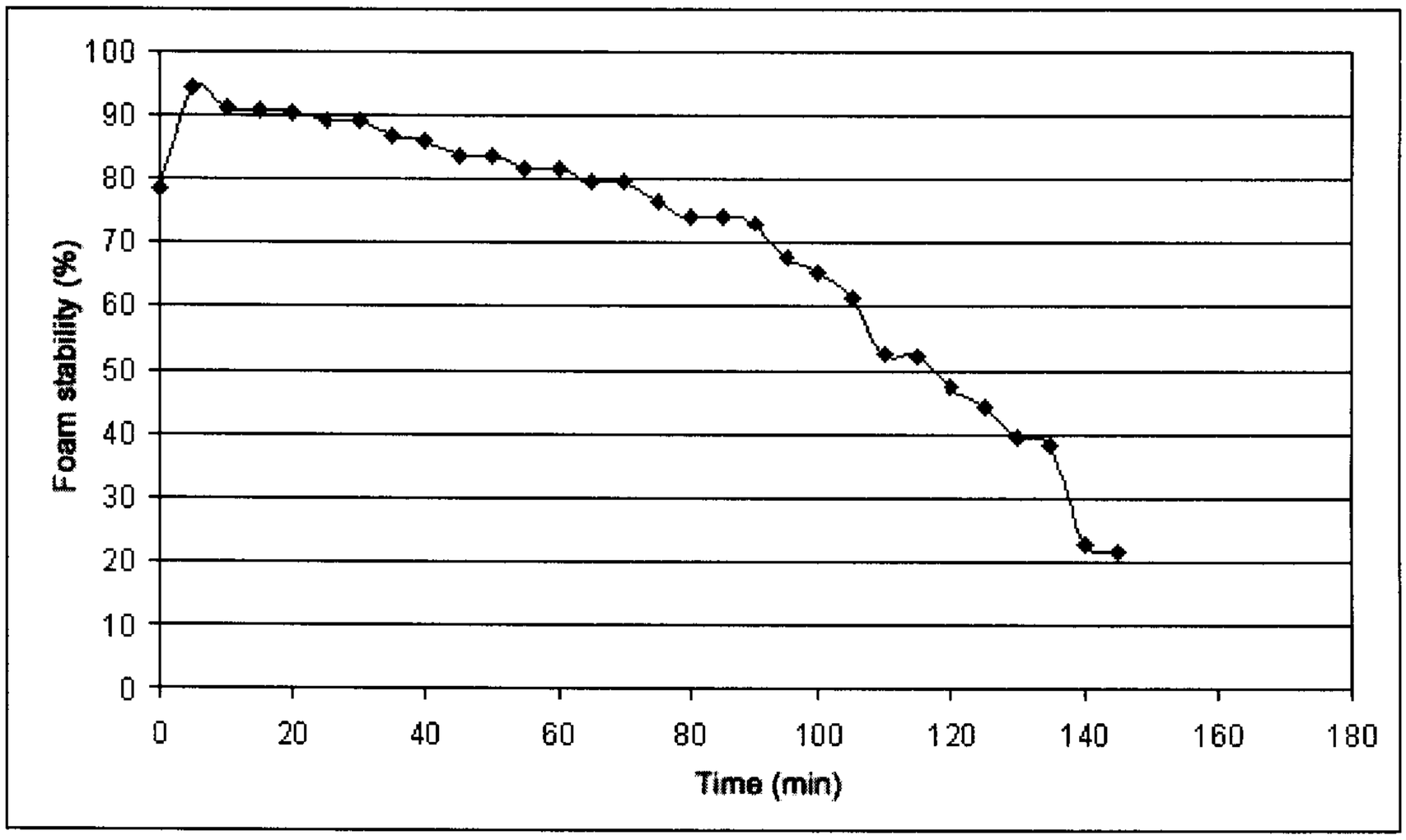

Foam stability (%)
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
140
160
180
Time (min)

Figure 19

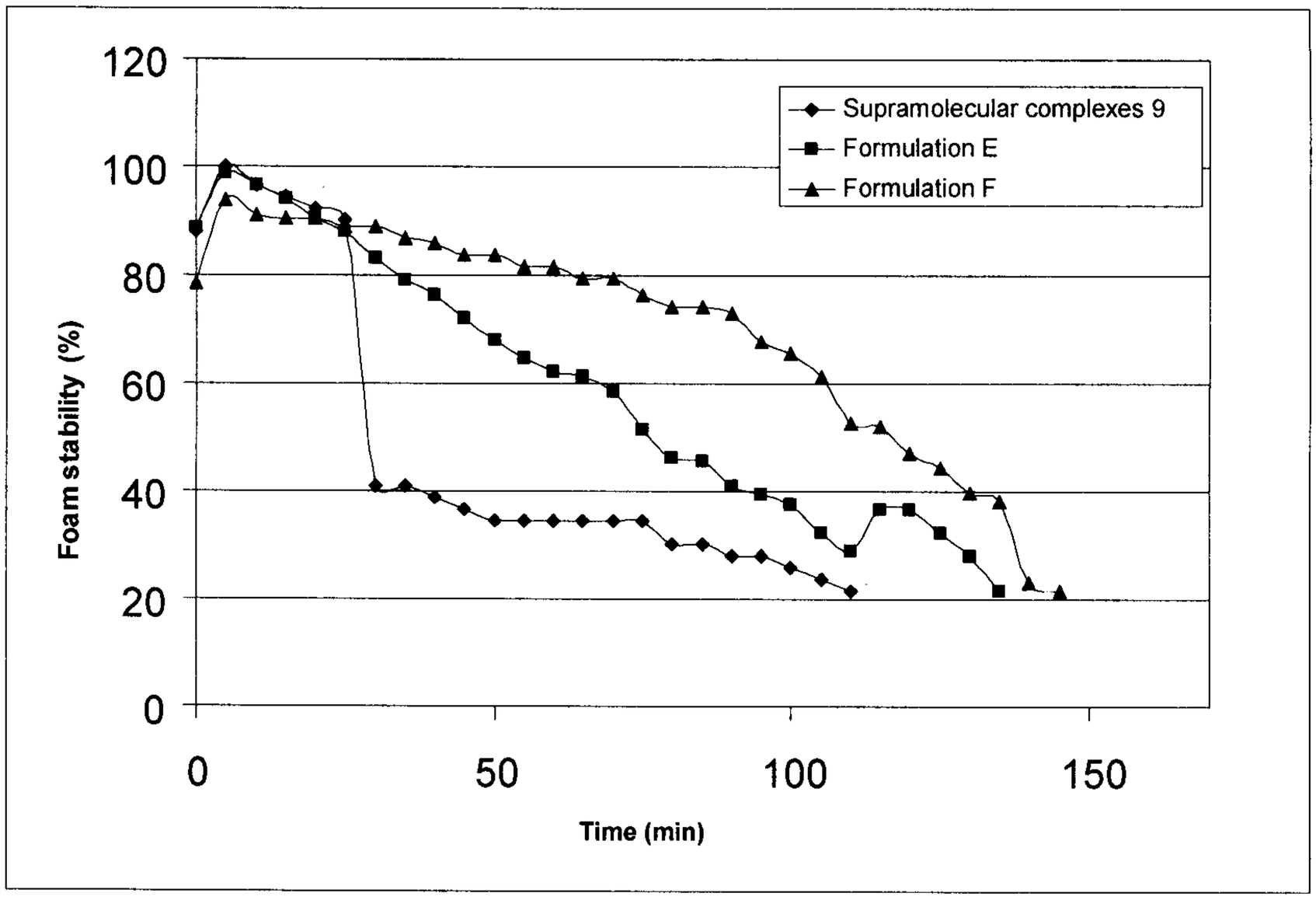

120
100
80
60
40
20
0
Foam stability (%)
0
50
100
150
Time (min)
Supramolecular complexes 9
Formulation E
Formulation F

Figure 20

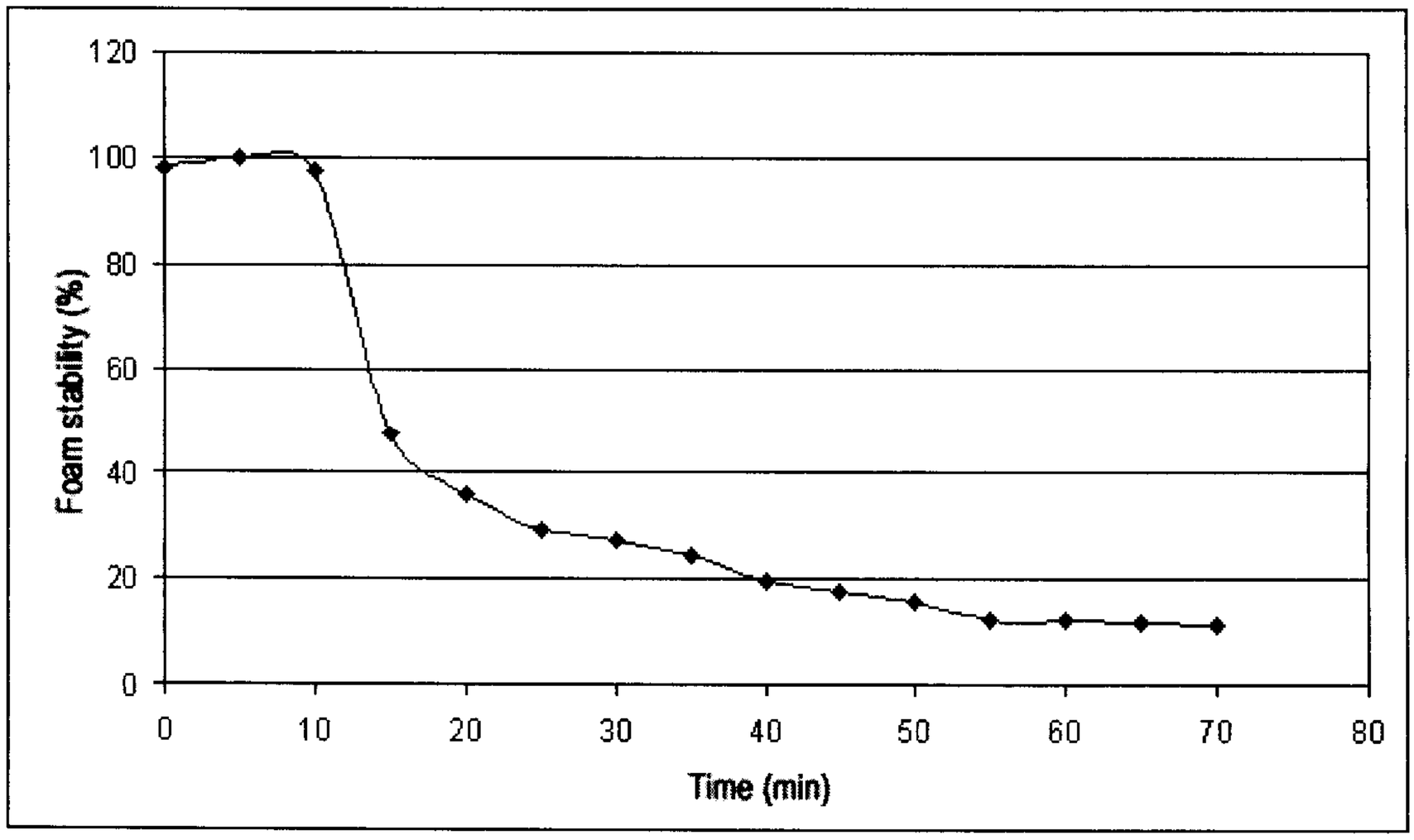

120
100
80
60
40
20
0
Foam stability (%)
0
10
20
30
40
50
60
70
80
Time (min)

Figure 21

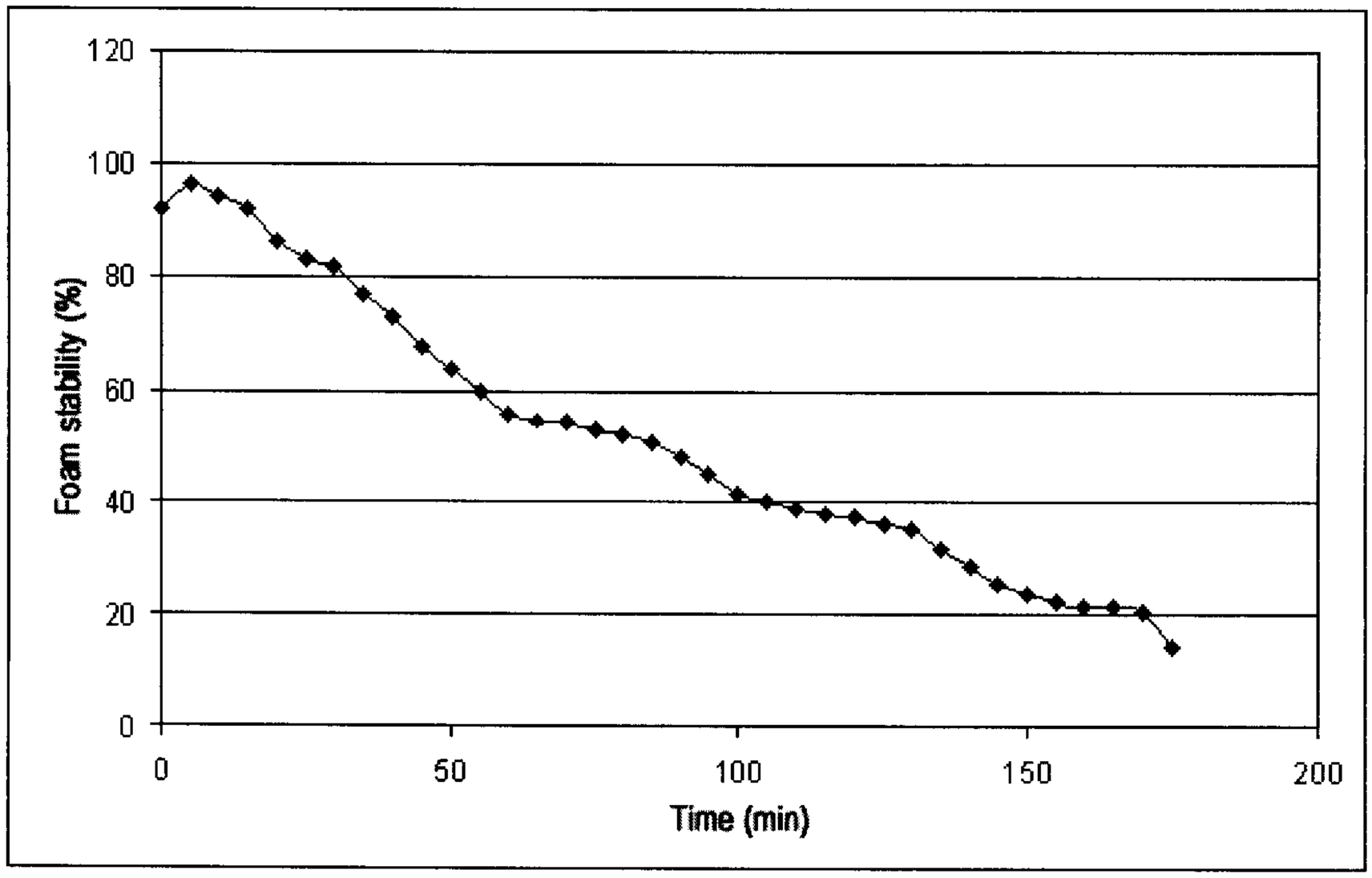


Figure 22

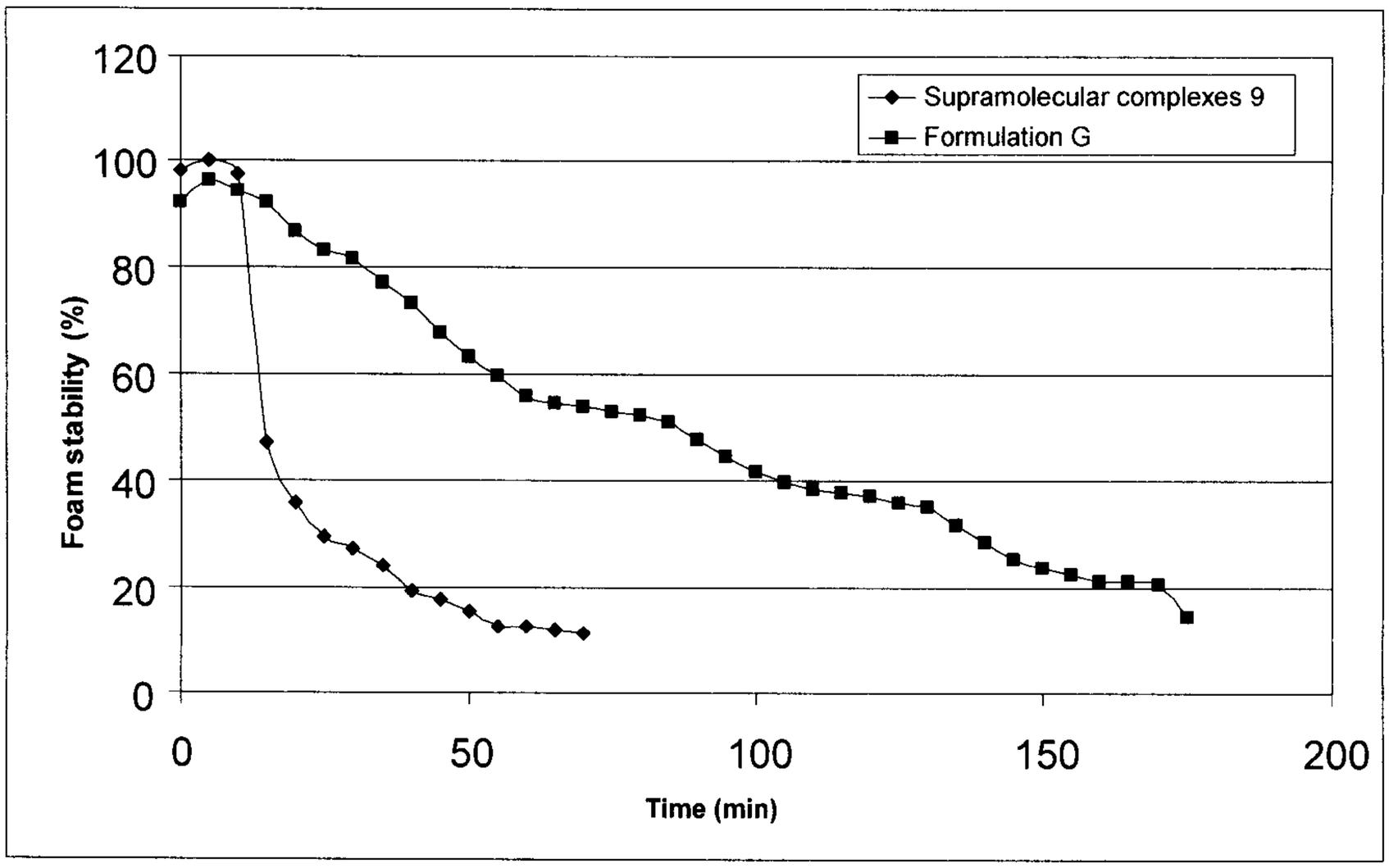

Supramolecular complexes 9
Formulation G
Foam stability (%)
120
100
80
60
40
20
0
0
50
100
150
200
Time (min)

Figure 23

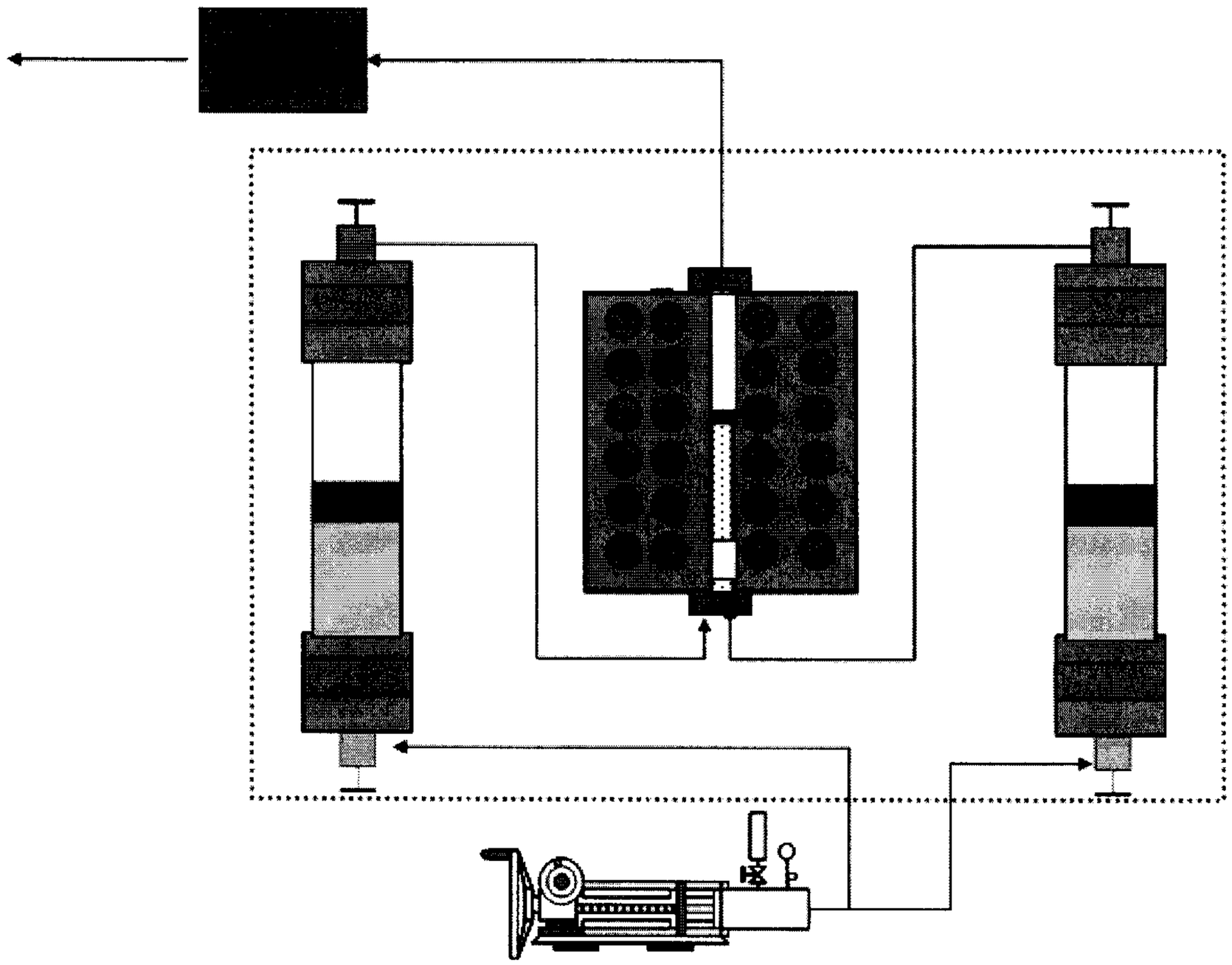


Figure 24

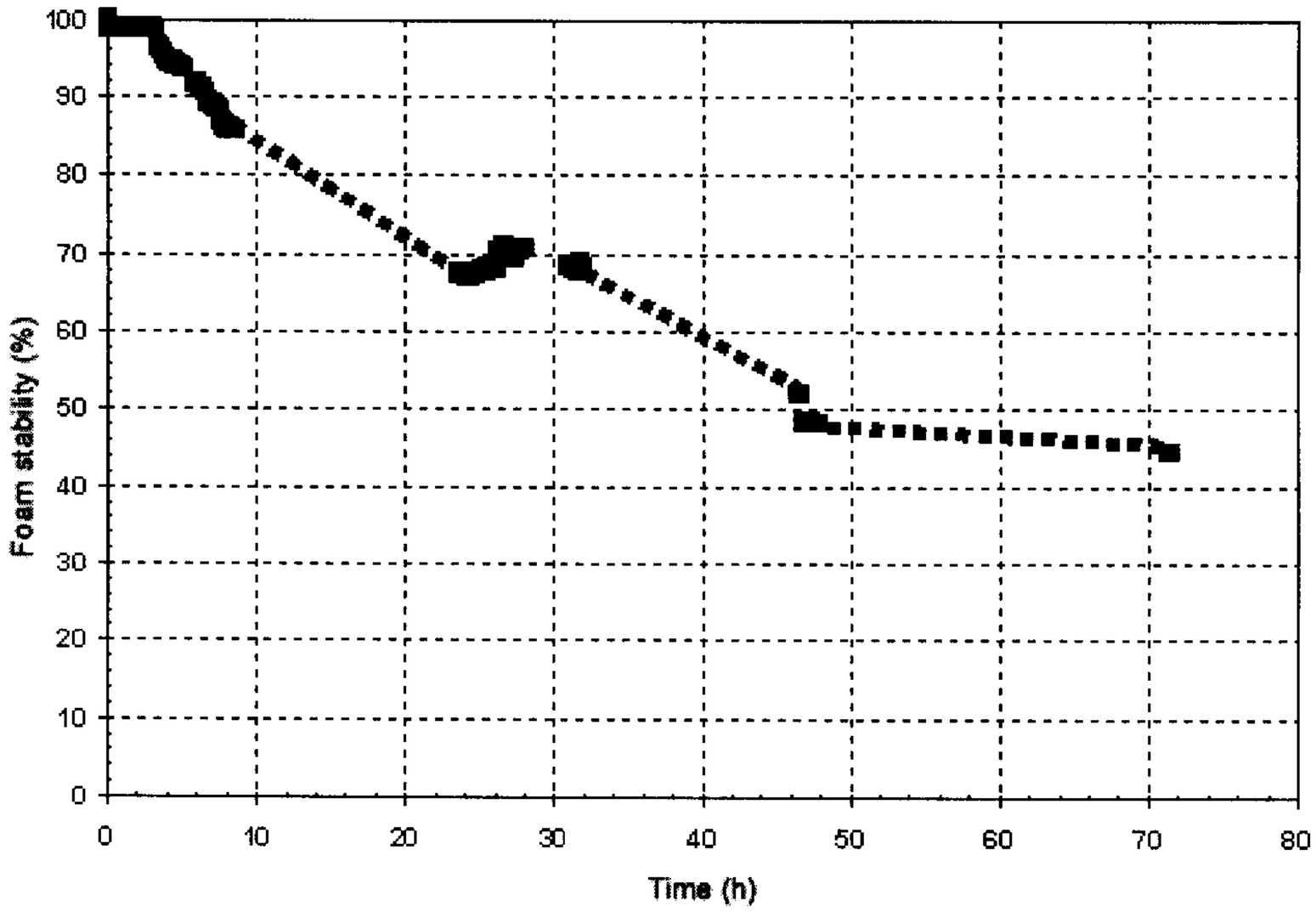

Foam stability (%)
Time (h)
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
80

Figure 25

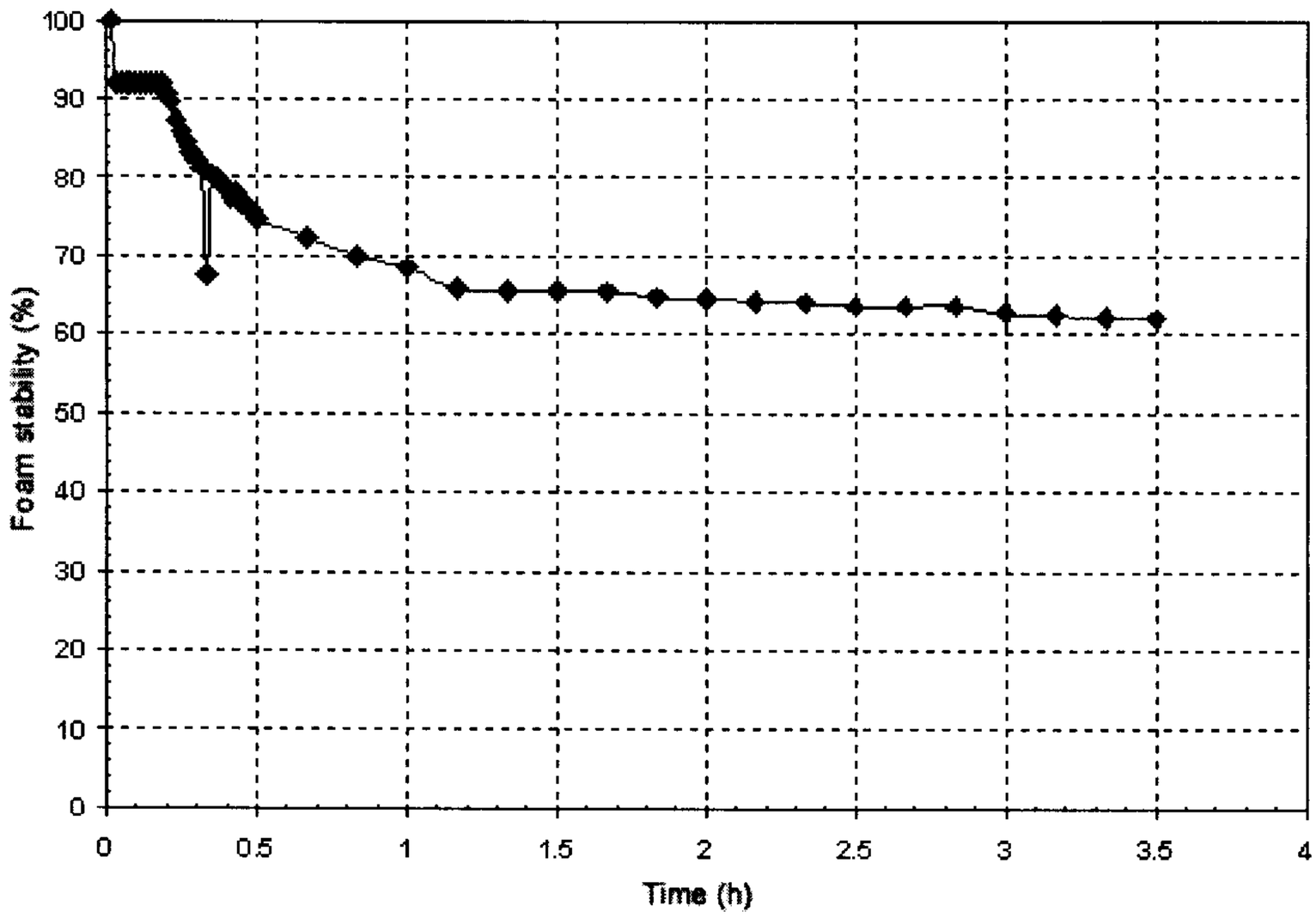

100
90
80
70
60
50
40
30
20
10
0
Foam stability (%)
0
0.5
1
1.5
2
2.5
3
3.5
4
Time (h)

Figure 26

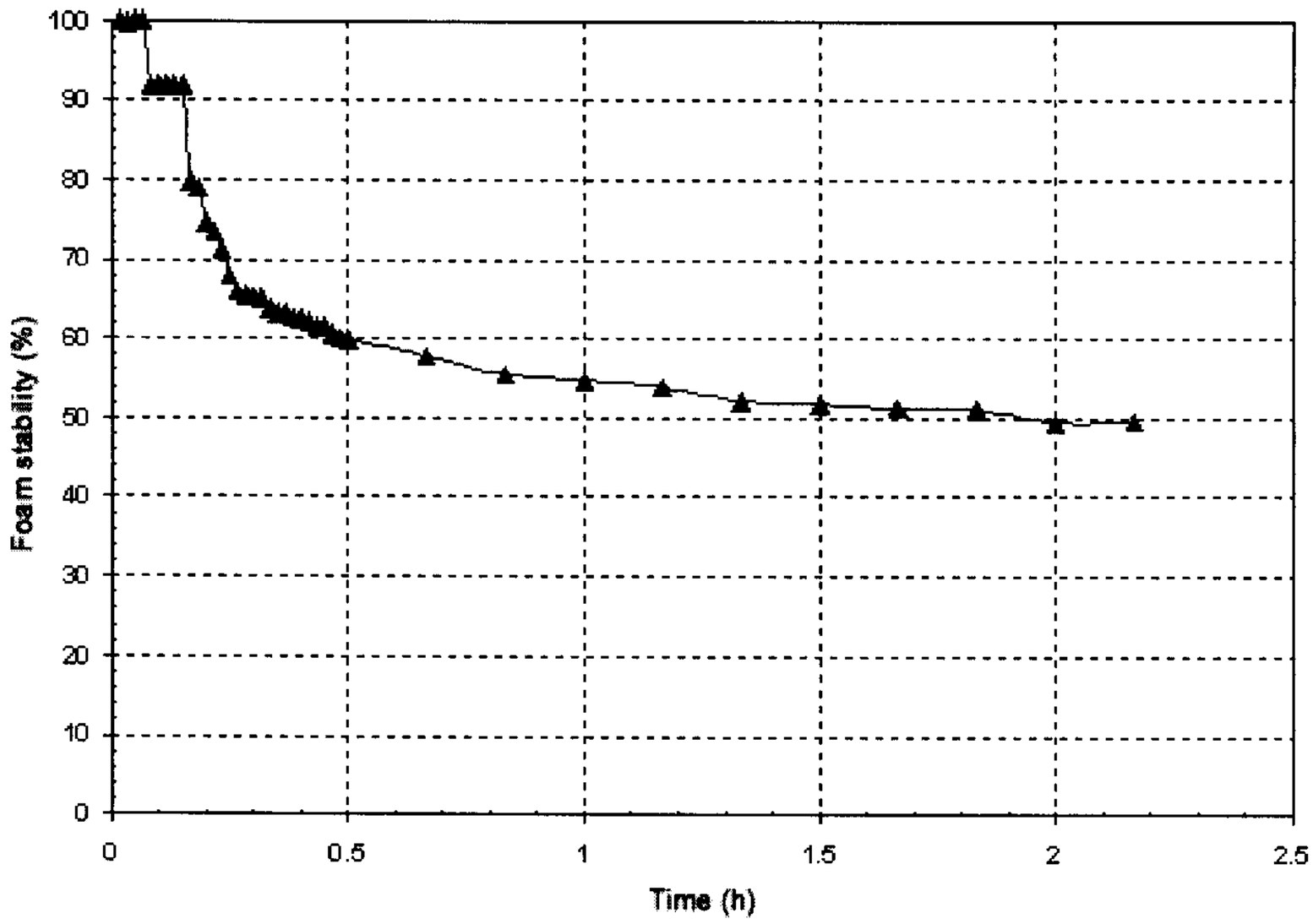


Figure 27

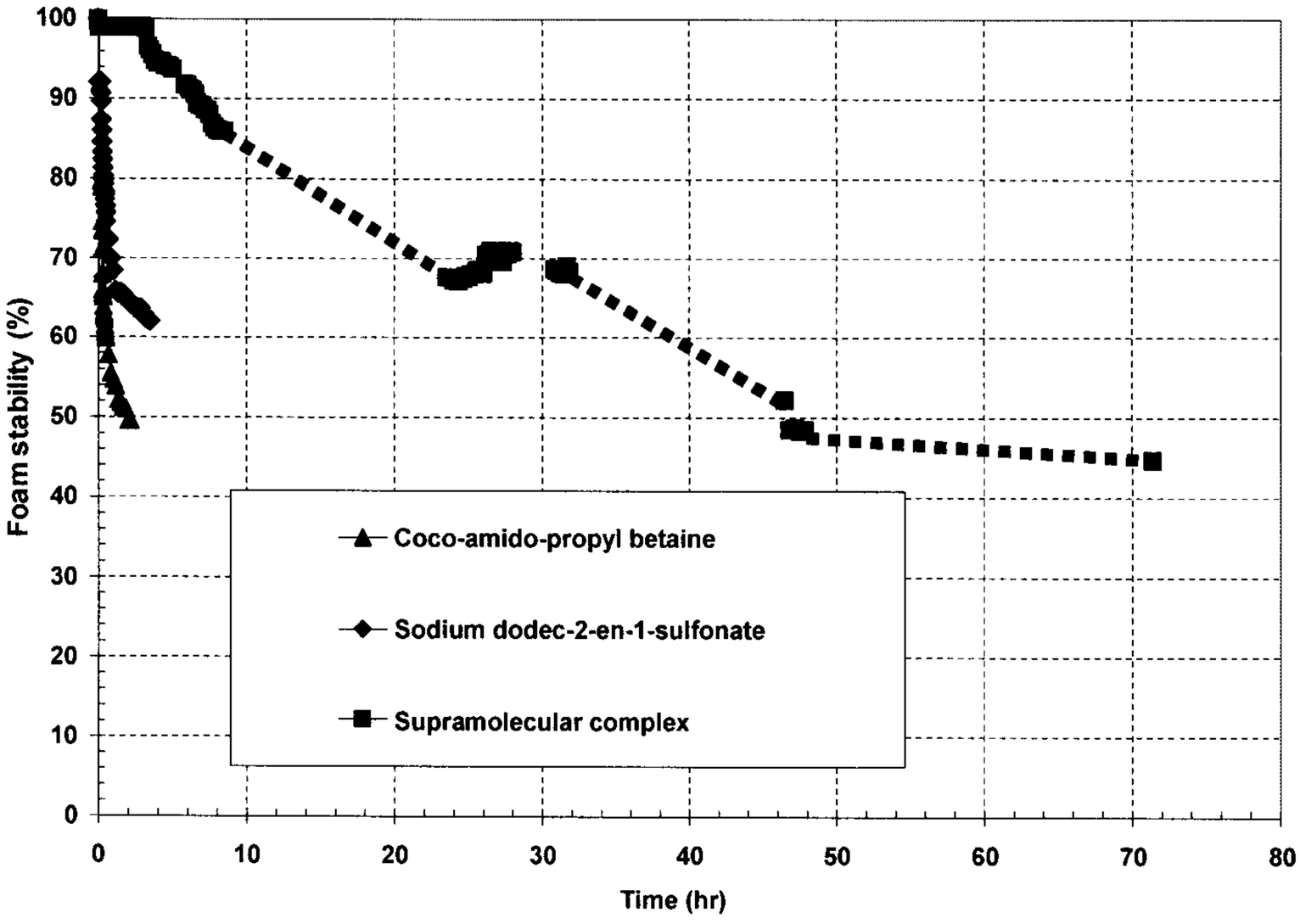

Foam stability (%)
Time (hr)
0
10
20
30
40
50
60
70
80
90
100
Coco-amido-propyl betaine
Sodium dodec-2-en-1-sulfonate
Supramolecular complex

Figure 28

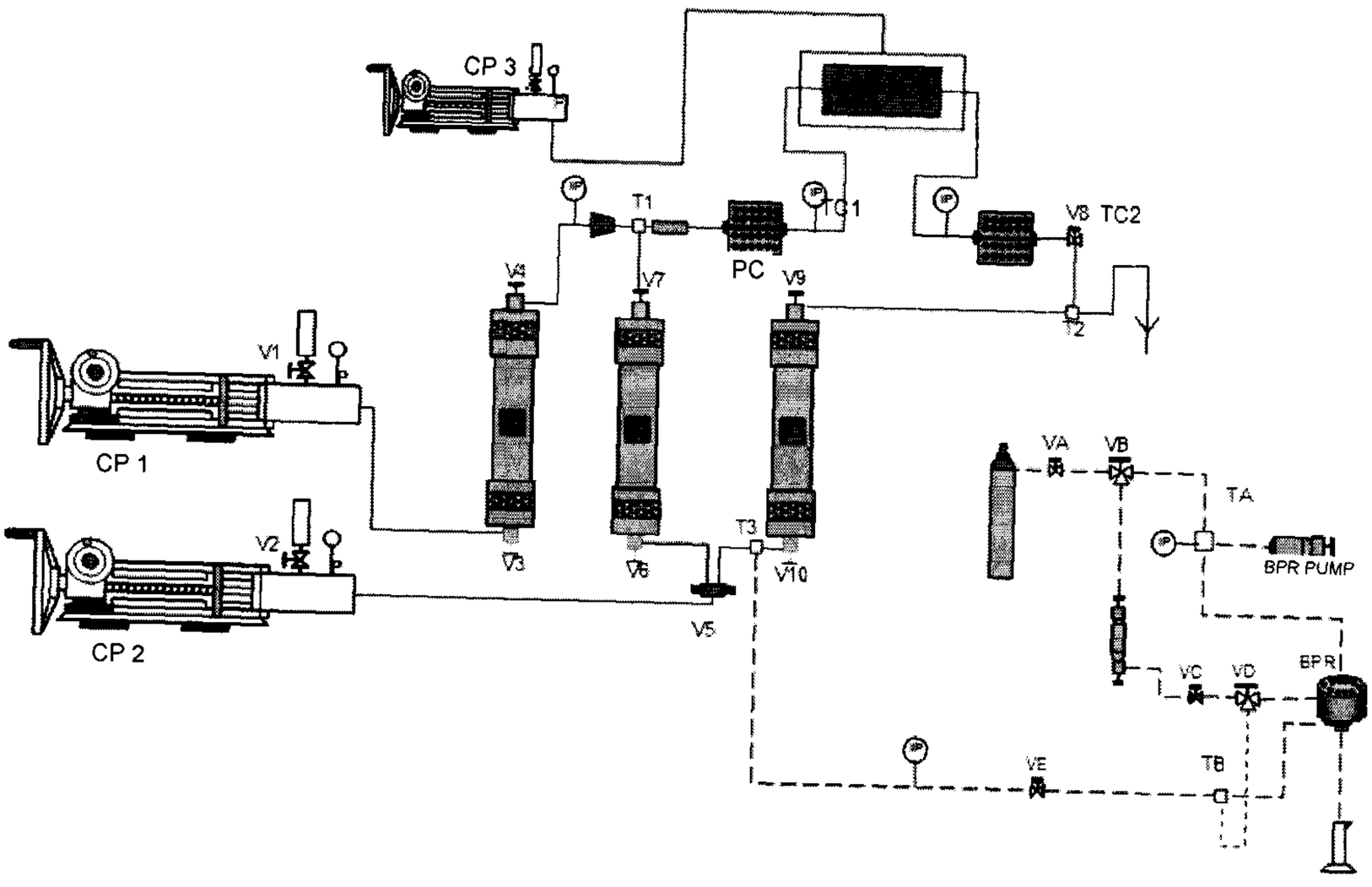

CP 3
T1
TC1
PC
V4
V7
V9
V8 TC2
T2
V1
CP 1
V2
CP 2
V3
V6
V10
T3
V5
VA
VB
TA
BPR PUMP
VC
VD
BPR
VE
TB

Figure 29

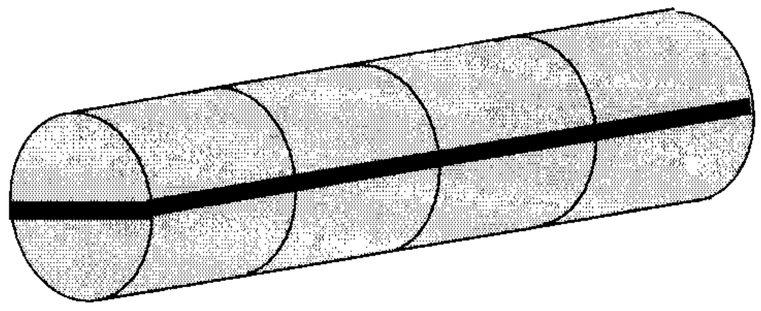


Figure 30

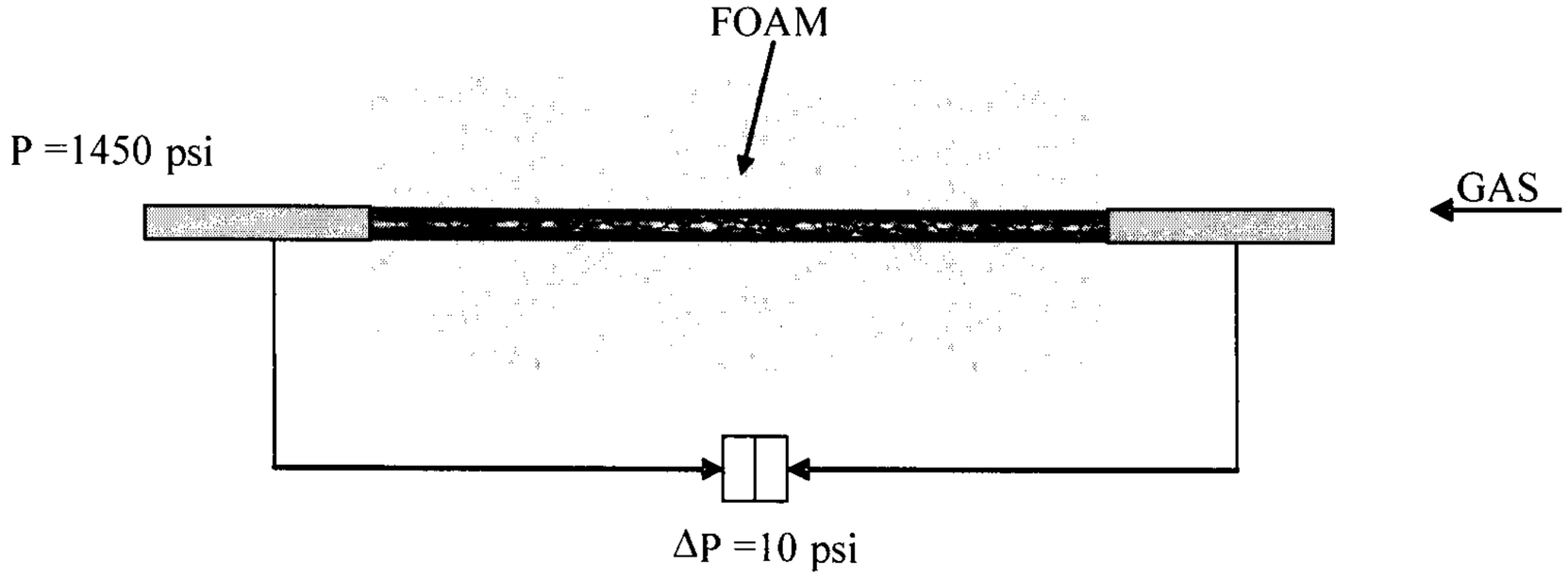
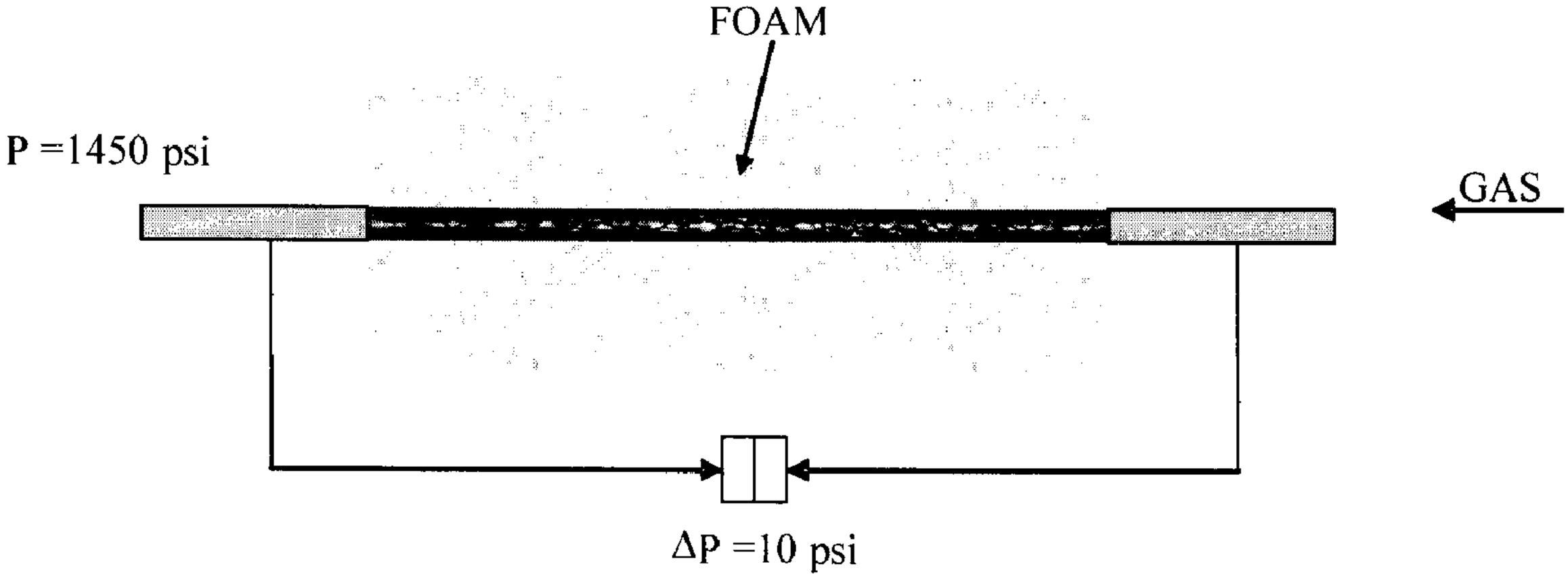


Figure 31


FOAM
P =1450 psi
GAS
ΔP =10 psi