Lab. de Formulación, Interfases,
Reología y Procesos
Tel: ++58(0)274-2402954 fax 2402957
http://www.firp.ula.ve

2012 PUBLICATIONS AND COMMUNICATIONS BY LAB. FIRP ASSOCIATES

QUINTERO L., CLARK D. E., JONES T. A., SALAGER J. L., FORGIARINI A.
In situ fluid formation for cleaning oil or synthetic oil based mud.
US Patent 8,091,645 B2 (January 10, 2012)
ABSTRACT: Nanoemulsions, macroemulsions, miniemulsions, microemulsion systems with excess oil and water or both (Winsor I, II or III phase behavior) or single phase microemulsions (Winsor IV) improve the removal of filter cakes formed during hydrocarbon reservoir well bore drilling with OBM. The macroemulsion, nanoemulsion, miniemulsion, microemulsion systems with excess oil and water or both or single phase microemulsion removes oil and solid from deposited filter cake. In one non-limiting embodiment, the emulsion system (e.g. single phase microemulsion, nanoemulsion, or other emulsions) may be formed in situ (downhole) rather than produced or prepared in advance and pumped downhole. Skin damage removal from internal and external filter cake deposition can be reduced.

QUINTERO L., JONES T. A., CLARK D. E., GABRYSCH A. D., FORGIARINI A., SALAGER J. L.,
Single phase microemulsions and in situ microemulsions for cleaning formation damage.
US Patent 8,091,646 B2 (January 10, 2012)
ABSTRACT: Single phase microemulsions (SPMEs) and in-situ formed microemulsions may be used to clean up and remove non-polar material from reservoir production zones of oil and gas wells. This clean up occurs by solubilization of the non-polar material into the microemulsion when the treatment fluid contacts the non-polar material. An in-situ nicroemulsion may be formed when one or more surfactant and a polar phase (e.g. water or brine) and eventually some small amount of organic phase, contacts the reservoir formation and solubilizes the non-polar material encountered in the porous media. The microemulsions ae effective for removing the formation damage caused by non-polar mterials which include, but are not necessarily limited to OBM, synthetic-based mud, paraffins, asphaltenes, emulsions, slugs, and combinations thereof.

QUINTERO L., SALAGER J.L., FORGIARINI A., PIETRANGELI G., BREGE J.
Efficient Displacement of Synthetic or Oil-based Mud and Transitional Phase Inversion.
1rst Int. Conference on Upstream Engineering and Flow Assurance. AIChE Spring Meeting
Houston, 04/04/2012
ABSTRACT: Effective displacement of a synthetic or oil-based mud (S/OBM) to completion brine is extremely important in order to minimize non-productive time (NPT), to lower brine filtration costs, reduce waste volume, to prevent cement failures and to reduce the risk of completion tool complications during the completion of a well. A good displacement spacer

system should remove the S/OBM and debris, prevent viscous emulsions or sludge, be compatible with the drilling fluid in order to prevent channeling and should completely water-wet all metal surfaces in no more than a single circulation of completion brine. The key spacer properties to obtain an effective displacement of the S/OBM are (1) high detergency or oil removal, (2) good mud/spacer compatibility without noticeable increase of viscosity at the fluids interface and (3) ability to change wettability of the rock and metal from oil-wet to water-wet.
Spacer fluids with such required properties need to have good microemulsification of the non polar components of the S/OBM and produce a transitional phase inversion from oil-continuous phase to water-continuous emulsion. This paper discusses the phase behavior of microemulsion spacer systems, the transitional phase inversion, and the interfacial properties that result in successful displacements of synthetic-based drilling fluids in deepwater applications.

SALAGER J.L., FORGIARINI A., ANTON R.E., QUINTERO L.
Available Know-how in Transforming an Emulsified Drilling Fluid to be removed from unwanted location into a low-viscosity Single Phase System.
Invited lecture, *1rst Int. Conference on Upstream Engineering and Flow Assurance. AIChE Spring Meeting* Houston, 04/04/2012.
ABSTRACT: Drilling fluids are generally emulsions, either O/W or W/O, with an aqueous phase containing various electrolytes and an oil phase ranging from hydrocarbons to polar oils. Such multiphasic systems are stabilized by surfactants and cosurfactants whose nature is related to the emulsion morphology. Stable emulsions should have an unbalanced generalized formulation which is also related to the phase behavior at equilibrium. If the drilling fluid tends to form a viscous multiphase in the casing void or to enter the porous medium and to plug it by capillarity, it has to be removed as a single phase system of the mesophase type. This usually requires the formation of a bicontinuous microemulsion with a surfactant system exhibiting the highest solubilization of both oil and water phases, a situation that takes place when the formulation is exactly balanced. Moreover this should also occur with an amount of surfactant as small as possible and this is yet an unsolved problem. Recent developments indicate that there are several trends toward performance improvement that can be used in parallel or together, and this is what has been used in practical case

SALAGER J.L., FORGIARINI A.
Emulsion Stabilization, Breaking and Inversion: Advantage or Inconvenience in Flow Assurance.
Invited lecture, *1rst Int. Conference on Upstream Engineering and Flow Assurance. AIChE Spring Meeting* Houston, 04/04/2012.
ABSTRACT: Emulsion type and stability are directly linked with the physico-chemical formulation, which controls the interfacial interactions of the surfactant with the oil and water phases. During petroleum production processes emulsions have to be stabilized, broken or inverted, and the formulation has to be adjusted to attain the required property. This is in particular the way to reach a proper rheology that insures the flow. If the formulation is not controlled unwelcome changes like phase inversion can take place and plug the porous medium or the pipeline through which a multiphase system is transported. Three specific cases still under development are discussed as critically depending on formulation: displacement in porous medium during surfactant flooding for enhanced oil recovery, heavy crude oil emulsified transport in pipeline, and control of gas hydrates slurry in deep subsea transportation

FORGIARINI A., RODRIGUEZ J., MARQUEZ L., CELIS M.T., SALAGER J.L.
Antioxidant activity of essential oils encapsulated in nanoemulsions.
Nanoformulation 2012, *7th Inform & FSTG Conference*, May 28-June 1, Barcelona Spain (2012)
ABSTRACT: The encapsulation of essentials oils using nano-emulsified systems has potential application in personal care products for antioxidant delivery systems. This work reports the formulation of oil-in-water nanoemulsions containing essential oils like rosemary and cypress in liquid paraffin. Paraffin and essential oils were characterized by their EACN (Equivalent Alkane Carbon Number) using the SAD (Surfactant-Affinity-Difference) generalized formulation concept. Nanoemulsions were prepared with a mixture of two nonionic surfactant calculated to adjust the proper SAD to produce the required phase transitions to use a low energy emulsification method. Nanoemulsions were characterized by droplet size, transmittance and stability. Antioxidant activity of pure essential oils and encapsulated in nanoemulsions and macroemulsion were studied by using the 2,2'-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging method. It was concluded that the antioxidant activity depend not only on the droplet size distribution, but also on the essential oil type.

SALAGER J.L., FORGIARINI A., BULLON J.
Surfactant Formulation to Reach the Ultralow Interfacial Tension required for Enhanced Oil Recovery.
Chap. 5. In *Topics in Colloidal Aggregation and Interfacial Phenomena*. M. Garcia Sucre, A Lozsan, A Castellanos-Suarez & J Toro-Mendoza Eds. Research Signpost, Kerala, India (2012) pp 125-160.
ABSTRACT: Surfactant-oil-water systems are likely to exhibit an interfacial tension low enough for enhanced oil recovery, only when a so-called optimum formulation is attained. This corresponds to a physicochemical condition that may be expressed as a correlation between the different variables that takes into account the nature of the components, as well as temperature and pressure. The quality of an optimum formulation may be defined by a performance index, related to the tension or the solubilization. Since Winsor's pioneering work in the 1950's, many studies dealing with the desirable surfactant structure, as well as with intermolecular and intra-molecular mixtures of surfactants, co-surfactants and other additives, have delivered guidelines to optimize the formulation to inject in a surfactant/polymer flooding. Although some issues are still under study, these discussed rules would help in developing satisfactory processes in the next years.

MARQUEZ N., BRAVO B., CHAVEZ G., YSAMBERTT F., SALAGER J.L.
Partitioning of fatty carboxylic acids and ethoxylated nonionic surfactants in microemulsion-oil-water systems.
Chap. 6. In *Topics in Colloidal Aggregation and Interfacial Phenomena*. M. Garcia Sucre, A Lozsan, A Castellanos & J. Toro-Mendoza Eds. Research Signpost, Kerala, India (2012) pp 161-200
ABSTRACT: The partitioning of surfactant species between oil and water depends on all physicochemical variables which are likely to alter the balance of affinity of the surfactant for the oil and water phases. Experimental data indicate how the logarithm of the partitioning coefficient varies with the nature characteristics of surfactant (degree of ethoxylation, alkyl chain length), the nature of both liquids (oil alkane carbon number, aqueous phase salinity), and the cosurfactant (lipophilic alcohol) content. The partitioning of surfactant in the oil-

water phases in a Winsor III system at optimum formulation is determined. The effect of different physicochemical variables in the partitioning of surfactant is discussed. Surfactant-oil-water systems in which the surface-active substance is a mixture of ethoxylated oligomer or an undissociated fatty acid (FA) and its soap salt, exhibit the typical phase behavior and the general emulsion phenomenology produced by a formulation scan.

SALAGER J.L., FORGIARINI A., ANTON R.E., QUINTERO L.
Available Know-how in Transforming an Emulsified Drilling Fluid to be removed from unwanted location into a low-viscosity Single Phase System.
Energy & Fuels **26**: 4078-4085 (2012)
ABSTRACT: Drilling fluids are generally emulsions, either O/W or W/O, with an aqueous phase containing various electrolytes and an oil phase ranging from hydrocarbons to polar oils. Such multiphasic systems are stabilized by surfactants and cosurfactants whose nature is related to the emulsion morphology. Stable emulsions should have an unbalanced generalized formulation which is also related to the phase behavior at equilibrium. If the drilling fluid tends to form a viscous multiphase in the casing void or to enter the porous medium and to plug it by capillarity, it has to be removed as a single phase system of the mesophase type. This usually requires the formation of a bicontinuous microemulsion with a surfactant system exhibiting the highest solubilization of both oil and water phases, a situation that takes place when the formulation is exactly balanced. Moreover this should also occur with an amount of surfactant as small as possible and this is yet an unsolved problem. Recent developments indicate that there are several trends toward performance improvement that can be used in parallel or together, and this is what has been used in practical case

SALAGER J.L., FORGIARINI A.
Emulsion Stabilization, Breaking and Inversion: Advantage/Inconvenience in Flow Assurance.
Energy & Fuels **26:** 4027-4033 (2012)
ABSTRACT: Emulsion type and stability are directly linked with the physico-chemical formulation, which controls the interfacial interactions of the surfactant with the oil and water phases. During petroleum production processes emulsions have to be stabilized, broken or inverted, and the formulation has to be adjusted to attain the required property. This is in particular the way to reach a proper rheology that insures the flow. If the formulation is not controlled unwelcome changes like phase inversion can take place and plug the porous medium or the pipeline through which a multiphase system is transported. Three specific cases still under development are discussed as critically depending on formulation: displacement in porous medium during surfactant flooding for enhanced oil recovery, heavy crude oil emulsified transport in pipeline, and control of gas hydrates slurry in deep subsea transportation

MERCADO R., SADTLER V., MARCHAL P., CHOPLIN L., SALAGER J.L.
Heteroflocculation of a cationic oil-in-water emulsion resulting from Fontainebleau's sandstone powder addition and its its implication with asphalt emulsion breakup.
Industrial Engineering Chemistry Research **51**: 11688-11694 (2012)
ABSTRACT: The use of asphalt emulsions for road fabrication is rapidly gaining in importance mainly due to energy savings, less environmental impact and better properties of the final product. However, the formulation of these emulsions still requires a better understanding, particularly concerning their breaking phenomena. When a cationic model emulsion is contacted

with a solid having a negative-charged surface, physicochemical driving forces result in the emulsion destabilization. As a consequence, a viscosity reduction of the remaining emulsion is observed, as well as the emulsion break-up through a heteroflocculation mechanism provided the solid surface is large enough. Emulsion systems at equilibrium, containing Cetylpyridinium Chloride (CPC), paraffin oil and Fontainebleau's sandstone powder and having different droplet sizes are studied. The results show that the dispersed oil fraction decreases after each addition of sandstone aliquots, and this depends on the concentration of CPC in the continuous phase of the emulsion. As the droplet size and distribution remain constant during the process, it is assumed that the emulsion heteroflocculation is the result of direct oil droplets adhesion on the sand surface, followed by their coalescence around the sand particles.

DELGADO-LINARES J.G., BULLON J.
Caracterización del petróleo. Un reto para el ingeniero moderno. [Spanish]
3er Congreso de Ingeniería de Petróleo, Gas, Química y Geológica (COINPEG 2012) Margarita Island, Venezuela. November 29 - December 2, 2012
ABSTRACT: **Petroleum characterization**. Most of petroleum refining processes depend on crude oil properties and composition; the potential of conversion in valuable products is a function of crude oil physical and chemical characteristics. For that reason, modern refinery engineer must know how to measure the mean properties of the crude oil to process, as well as how to correlate these properties with its behavior under several conversion and separation operations. Crude oil characterization evolves from practical laboratory procedures (ASTM methods) to very complex thermodynamic methods for property estimation. Additionally, in enhanced oil recovery it is necessary to characterize the crude oil using typical concepts from the formulation of surfactant-oil-water systems.

DELGADO N., YSAMBERTT F., CHAVEZ G., BRAVO B., MARQUEZ N., BULLON J.
Síntesis asistida por microondas de derivados acilados de lignina de diferentes masas molares con posible actividad superficial. [in Spanish]
Avances Ciencias e Ingenieria **3**: 19-31 (2012)
ABSTRACT: **Microwave assisted synthesis of acylated lignin derivatives of different molar mass with possible surface activity.** Lignins of different molar masses were esterified using microwave radiation and the surface activity of the derivatives obtained were evaluated. The lignin was fractionated by ultrafiltration using ceramic membranes of 15 and 8 kDa. Succinic anhydride and glutaric anhydride were used to modify the lignin. The surface activity of the derivatives was evaluated by measuring the surface tension. FTIR spectra showed the incorporation ofcarboxylic acid-ester groups in lignin. Esterified products decreased the surface tension between 10-20% with respect to the original lignin, and this effect was greater for glutaric anhydride esterified products at high concentrations. The incorporation of new acid-ester groups in the lignin structure provides a higher amphiphilic character to lignin, due to the presence of new polar functional groups that allow the adsorption on the surface minimizing the attraction forces within the liquid.

AVENDAÑO J., PANNACCI N., HERZHAFT B., GATEAU P., COUSSOT P.
Normal Stresses and Interface Displacement: Influence of Viscoelasticity on Enhanced Oil Recovery Efficiency.
Oil & Gas Science & Technology _ Rev IFP Energies Nouvelles **67**: 921-930 (2012)

ABSTRACT: One of chemical Enhanced Oil Recovery (EOR) methods consists in injecting aqueous solutions of polymers into the reservoir in order to improve mobility ratio between the injected fluid and the remaining oil. This "polymer flooding" process is usually only characterized with the low shear viscosity of the injected fluid, even if these aqueous solutions are strongly shear thinning and may show high elastic properties evidenced by normal stresses appearance. In order to study the mechanisms at the interface level, we develop simple model experimentations with the goal of quantifying the influence of viscoelastic properties on fluid displacement in a simple geometry.
For this purpose, we propose and characterize a model fluid formulation, for which elastic and viscous effects can be tuned systematically. We study then the displacement of a viscous oil by a Newtonian non elastic, a viscoelastic or a purely shear thinning fluid in a two dimensional flow cell. Observing the shape of the interface between aqueous fluids and displaced oil permits to appreciate viscoelasticity effects on the displacement. Using model geometries and controlled rheology fluids, we show that viscoelastic fluids tend to better displace immiscible liquids than Newtonian fluids and that those effects are closely related to the apparitions of normal stresses independently of shear thinning property or variation of interfacial tension as soon as viscous effects govern the flow.

DELGADO-LINARES J.G., PEREIRA J.C., RANGEL A., SALAZAR F., GUEVARA M., FORGIARINI A., BULLON J.

Efecto de la adición de moléculas anfifílicas sobre las propiedades de la película de asfaltenos en la interfase aire-agua.

Revista Ingeniería Univ Carabobo **19** (2) : 16-24 (2012)

ABSTRACT: Using Langmuir isotherms it has been studied the behavior of film of asphaltenes extracted from Ayacucho crude oil (Orinoco oil belt) at air-water interface. The effect of surfactants like stearic acid and dimethyl stearyl ammonium chloride on asphaltene films was determined. Respect to this, it was found out the stearic acid increases the film compressibility in all tested proportions; on the other hand, the chloride increases the film compressibility in an asphaltenes: surfactant ratio of 7:3 and 1:1, when this ratio is 3:7, the film compressibility decreases in comparison to the pure asphaltene fraction

QUINTERO L., CLARK D.E., CARDENAS A.E., SALAGER J.L., FORGIARINI A., BAHSAS A.H.

Dentritic surfactants and extended surfactants for drilling fluid formulations.

US Patent Application 2012/0241220A1 (September 27, 2012)

ABSTRACT: Modified surfactants may be added to an oil-based drilling fluid where the modified surfactant is selected from the group consisting of an extended surfactant, a dentritic surfactant, and a combination thereof. These oil-based drilling fluids may be used for drilling a well through a subterranean reservoir, while circulating the oil-based drilling fluid through the well-bore. The oil-based drilling fluid may include at least a modified surfactant, at least one non-polar continuous phase, and at least one polar non-continuous phase. The modified surfactant may have propoxylated/ethoxylated spacer arm extensions. The modified surfactant may have intramolecular mixtures containing hydrophilic and lipophilic portions. They attain high solubilization in the oil-based drilling fluid and may be, in some instances, insensitive to temperature making them useful for a wide variety of oil types.

DELGADO-LINARES J.G., PEREIRA J.C., RANGEL A., SALAZAR F., GUEVARA M., FORGIARINI A., BULLON J.

Efecto de la adición de moléculas anfifílicas sobre las propiedades de la películas de asfaltenos en la interfase aire-agua. [Spanish]

Revista Fac. Ing. Univ Carabobo **19** (2): 16-24 (2012)

ABSTRACT: **Effect of addition of amphiphilic molecules on asphaltene film properties at air-water interface.** Using Langmuir isotherms, it has been studied the behavior of film of asphaltenes extracted from Hamaca crude oil (Orinoco oil belt) at air-water interface. The effect of amphiphilic molecules as stearic acid and dimethyl stearyl ammonium chloride on asphaltene films was determined. Respect to this, it was found out the stearic acid increases the film compressibility in all tested proportions; on the other hand, the chloride increases the film compressibility in an asphaltenes:amphiphile ratio of 7:3 and 1:1, when this ratio is 3:7, the film compressibility decreases in comparison to the pure asphaltene fraction.

DAGERT M., DELGADO-LINARES J.G., SALAZAR F., PEREIRA J.C., BULLON J., GUEVARA M.

Efecto del tensioactivo y de la naturaleza del solvente en la formación de películas de asfaltenos sobre agua. [Spanish]

2do Congreso Nacional de Química del Petróleo (II CNQP 2012) Barquisimeto, Venezuela. November 6-9, 2012

ABSTRACT: **Effect of surfactant and solvent nature on the formation of asphaltene film at water interface.** During crude oil extraction and production, asphaltene fraction is adsorbed at the water-oil interface creating stable emulsions. Asphaltene film properties were studied through the Langmuir trough technique, which allows to determine the surface pressure variation as a function of the molecular area. The aromaticity effect of solvent on asphaltene films was studied dissolving a fixed amount of asphaltenes in different organic solvents (toluene, benzene and cyclohexane) and measuring the variation of film compressibility in each case. Results demonstrated that the asphaltene film rigidity decreases when the solvent aromaticity increases. Furthermore, the film compressibility was evaluated under addition of a nonionic surfactant (ethoxylated nonyl phenol with four ethylene oxide groups). It was found that there is a strong interaction between the asphaltene fraction and surfactant molecules; this interaction produces a non-monotonic variation in the film compressibility, which exhibits a maximum at a surfactant concentration of 50 ppm.

DELGADO-LINARES J.G., FORGIARINI A., BARÓN J.

Efecto de los asfaltenos sobre la espumabilidad de sistemas no acuosos

2do Congreso Nacional de Química del Petróleo (II CNQP 2012) Barquisimeto, Venezuela. November 6-9, 2012 [Spanish]

ABSTRACT: **Effect of asphaltenes on the foamability of non-aqueous systems.** Foam generation produces severe problems in crude oil production processes. This work evaluates the effect of asphaltene (from Ayacucho crude oil) addition on the foamability of non-aqueous systems in which toluene and toluene- paraffin mixtures were used as solvent. It was shown that the system foamability (foam height) is proportional to the asphaltene content. Additionally, foam height reaches a maximum at a specific solvent aromaticity (30 vol. % of toluene in a toluene-paraffin mixture), which indicates that the asphaltene aggregation state influences the foamability of oily systems.

PIERLOT C., ONTIVEROS J.F., TAKAHASHI H., CATTE M., MOLINIER V., SALAGER J.L., AUBRY J.M.

Classification of esters oils by EACN scale using HLD method on (CiEj)/Oil/Water systems.

International Association of Colloid and Interface Scientists, Conference IACIS, May 13-18, 2012. Sendai (Japan)

ABSTRACT: The phase's behaviours of 10 $C_{10}E_4$/Ester/Water systems are investigated in terms of their fish-tail. The temperature and concentration of transition from Winsor III to Winsor WIV behaviour (T*,C*) are reported to calculate, using the Hydrophilic–Lipophilic Deviation (HLD) approach, their Equivalent Alkane Carbon Number (EACN). The influence of the structure of the esters: alcohol chain / acid chain lengths and ester's group position, have been clarified qualitatively. Fish diagrams are entirely developed to isopropyl myristate, glycerol trioctanoate and bis 2 ethylhexyl adipate in order to compare mono, di and triester. Conductivity and rheological experiments will be investigated to see the correlation between T* and the phase inversion temperature.

updated December 31rst, 2012