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# *2011 PUBLICATIONS AND COMMUNICATIONS BY LAB. FIRP ASSOCIATES*

**ZERPA L.E., SALAGER J.L., KOH C.A., SLOAN E.D., SUM A.K.**
Surface chemistry and gas hydrates in flow assurance.
*Industrial and Engineering Chemistry Research*. **50** :188-197 (2011)
*ABSTRACT:* A review of surface chemistry concepts is presented, with the principal objective of identifying interfacial phenomena and surface chemistry interactions involved in gas hydrate formation and agglomeration in oil and gas pipelines. There are five types of interfaces where gas hydrates may form and aggregate: gas/liquid, liquid/liquid, gas/solid, liquid/solid, and solid/solid; where the gas is the hydrocarbon gas, liquid is either oil, water or condensate, and solid is either gas hydrate or the pipe wall surface. A review of fundamental interfacial concepts can help create a better understanding of phenomena at these interfaces, and can help industry move from hydrate prevention to risk management. Two areas of surface chemistry have been selected to illustrate the concepts and mechanisms associated with these systems: surfactants and emulsions. Examples from the literature pertaining to gas hydrates are presented for each system

**PARUTA-TUAREZ E., SADTLER V., MARCHAL P., CHOPLIN L., SALAGER J.L.**
Making Use of the Formulation-Composition Map To Prepare Highly Concentrated Emulsions with Particular Rheological Properties
*Industrial Engineering Chemistry Research* **50**: 2380-2387 (2011)
*ABSTRACT:* The effects of the formulation and dispersed-phase weight fraction on rheological properties of highly concentrated water-in-oil emulsions are reported. Because the surfactant concentration is kept constant, emulsion characteristics may be represented on a formulation-composition bidimensional map. The formulation variable is the hydrophilic-lipophilic balance (HLB) number of the nonionic surfactant or surfactantmixture which ranges from 4.3 to 10. Highly concentrated water-in-dodecane emulsions are prepared using a semibatch process, with a dispersed-phase weight fraction ranging from 0.90 to 0.98. Two major effects are observed in relation to the formulation influence: First, elastic modulus (G0) remarkably decreases in the vicinity of optimum formulation whenever the affinity of the surfactant for the oil and water phases is exactly balanced (HLB = 10.5). Second, the elastic modulus value passes through a maximum, concomitant to a minimum drop size, at some distance of the so-called optimum formulation (HLB = 7.7). Hence, the use of a bidimensional formulation-composition map allows one to control and to modulate the final rheological properties of highly concentrated emulsions.

**VILLAREAL A. M., FERNANDEZ C., FORGIARINI A., MARQUEZ L., NIELLOUD F., SALAGER J.L.**

Nanoencapsulation de filtres solaires via nanoémulsions (Fr)

*Cahier de Formulation* Procédés et formulation au service de la santé, Durand A., Canselier J.P. Eds., **15**: 5-18. EDP Sciences, Paris (2011)

*ABSTRACT:* Nanocapsules are produced by a sequence of processes involving a phase transition and a chemical reaction. The starting system is an inverse micellar solution of surfactant in an oil phase which, when contacted with water, becomes a lamellar liquid crystal. When more water is added to produce a two-phase system, the liquid crystal stabilizes the formed O/W nanoemulsion. The pH of the aqueous phase is then shifted to promote the a polimerization reaction at the drop surface to generate the capsule wall. An example of this sol-gel process is described, e.g. the encapsulation of sunscreen substances.

**GALINDO J., SADTLER V., CHOPLIN L., SALAGER J.L.**

Mécanismes d'inversion de phase catastrophique lors de l'émulsification d'huiles visqueuses (Fr)

*Cahier de Formulation* Procédés et formulation au service de la santé, Durand A., Canselier J.P. Eds., **15**: 32-48. EDP Sciences, Paris (2011)

*ABSTRACT*: L'inversion de phase catastrophique correspond au changement de type d'une émulsion, d'une morphologie eau dans huile vers une morphologie huile dans eau ou *vice versa*. Elle résulte de la coalescence simultanée des gouttes de la phase disperée à l'approche d'une fraction d'empilement critique. Phénomène généralement non désiré lors de procédés classiques d'émulsification, il peut être mis à profit pour des applications spécifiques telles que la mise en émulsion de produits visqueux. La formation d'émulsions multiples intermédiaires est une étape accélérant l'inversion de phase catastrophique en augmentant le volume apparent de la phase dispersée et ce, même dès le rajout de faible quantité de cette phase. La mise en évidence expérimentale de cette étape est par contre délicate compte tenu de la forte instabilité de ces émulsions multiples. L'utilisation d'une phase huileuse visqueuse nous a permis d'obtenir des émulsions de différentes morphologies, suffisamment stables pour être observées en microscopie optique au travers d'un écoulement du type "squeezing flow ", permettant ainsi le suivi de l'évolution de l'inversion.

Nous avons pu clairement observer la formation d'émulsions multiples h/E/H, processus favorisé par la viscosité de la phase huileuse, permettant ainsi d'obtenir des inversions de phase pour des ajouts très faibles de quantités d'eau, conduisant ainsi à la formation d'émulsions H/E finales très concentrées (environ 90% de phase dispersée). L'inversion de phase résulte d'un mécanisme d'agglomération-coalescence qui, par établissement d'un réseau au sein du milieu, induit la propagation de l'inversion dans l'ensemble du système à l'approche de la fraction d'empilement critique. Nous avons pu observer également l'aboutissement complet ou partiel du phénomène d'inversion en fonction de la distribution de tailles de gouttes avant l'inversion et à la présence d'émulsions supermultiples ou multiples complexes (émulsions multiples où les gouttelettes encapsulées contiennent, elles aussi, d'autres petites gouttelettes piégées).

**PARUTA E., SADTLER V., MARCHAL P., CHOPLIN L., MARFISI S.**

Influence de la formulation optimale et de la fraction de phase dispersée sur le comportement rhéologique des émulsions gels (Fr)

*Cahier de Formulation* Procédés et formulation au service de la santé, Durand A., Canselier J.P. Eds., **15**: 71-80. EDP Sciences, Paris (2011)

*ABSTRACT*: Dans ce travail, nous avons étudié l'influence de la formulation optimale et de la

fraction de phase dispersée sur le comportement rhéologique des émulsions gels du type eau dans huile (E/H). La concentration totale entensioactifs étant constante pour les formulations testées, le comportement rhéologique des émulsions gels peut être représenté sur une carte bidimensionnelle formulation-composition. Des émulsions eau dans dodécane ont été préparées en utilisant des mélanges de tensioactifs non ioniques pour obtenir des valeurs moyennes de *HLB* comprises entre 4,3 et 10. Ces émulsions ont été élaborées, par un procédé semi-batch, en faisant varier la fraction de phase dispersée de 0,90 à 0,98. Pour toutes les formulations et compositions étudiées, le module élastique diminue exponentiellement en fonction du temps pendant les quatre premiers jours après la préparation, puis il demeure constant. Dans le cas des émulsions élaborées à *HLB* = 10, les modules élastiques sont toujours très faibles, par rapport aux autres formulations et ce, quelle que soit la fraction de phase dispersée. Ce comportement peut être expliqué par la proximité de la formulation optimale (*HLB* = 10,4), et en particulier par la diminution de la tension interfaciale à l'approche de cette formulation.

**PEREIRA J. C., DELGADO-LINARES J. G., BRIONES A., GUEVARA M., SCORZZA C., SALAGER J.L.**

Effect of solvent nature and dispersant performance on asphaltene precipitation from diluted solutions of unstable crude oil.

*Petroleum Science and Technology* **29**: 2432-2440 (2011)

*ABSTRACT :* The asphaltene precipitation kinetics was studied on El Furrial crude oil from western Venezuela, which is known to exhibit serious problems. A Turbiscan backscattering apparatus was used to evaluate the precipitation of asphaltenes with different solvents. The transmittance variation with time is studied as the crude is diluted with heptane, pentane and cyclohexane. Alkane containing systems exhibit a two stage behavior, whereas only one is found when diluting with cyclohexane. Dispersing agents were tested by using the precipitate height as a criterion of effectiveness. Results are reported for ethoxylated nonylphenols, toluene parasulfonic acid, and a commercial dispersant.

**SALAGER J.L., FORGIARINI A., MARQUEZ L.**

Understanding of extended surfactant intramolecular mixture behavior to enhance solubilization for a variety of applications.

*8th World Surfactant Congress CESIO,* OR80. Vienna, Austria. June 6-8, 2011

*ABSTRACT:* Surfactant mixing has been proposed in the past 50 years as a way to improve solubilization performance, in cleaning formulas, enhanced oil recovery, and food procesing among other applications. There are several way to use mixing for improving solubilization, particularly by fine tuning inter or intramolecular amphiphilic blending in bicontinuous microemulsions systems. There are essentially two inherent limits in the mixing tricks. The first one is the conflict between a higher molecular size in the tail and a better solubility in water, to increase solubilization and avoid precipitation at the same time. The second one is that the introduction of different surfactants or cosurfactants and additives like lipophilic and hydrophilic linkers, is likely to produce fractionation of the species, hence uncontrolled formulation at interface.

Fastening together the mixture components in a single molecule avoids both the precipitation and fractionation disadvantages, and has been the goal of the so-called extended surfactant structure, which contains an intermediate polarity spacer between the head and tail groups. Recent investigations on extended surfactants are showing new properties which are sometimes different and even opposite to the usual trends with conventional surfactants. The sequence organization

of a non uniform intermediate spacer has a strong effect on the behavior. The polypropylene spacer is supposed to lay in the oil phase, but it is somehow hydrated, thus resulting in a nonionic type variation with temperature in spite of an anionic head group. Mixing extended surfactants with conventional ones allows to separate the formulation and solubilization effects, which results in an easy way to set the optimum formulation for a given application These newly understood properties allow extended surfactants to be a potential novel solution in wide-ranging applications such as industrial detergency, enhanced oil recovery, petroleum well unplugging, drilling cuttings cleaning, crude oil dehydration, agricultural applications, foodstuffs and cosmetics.

**KADJIAN S. R., ZAMORA F., GARZA T., MARQUEZ de SANTIS L., SALAGER J. L.**
Methods for gas well treatment.
US Patent Application Publication 2011/0183872A1 (Jul. 28, 2011)
Methods for using a microemulsion system are disclosed which comprises a solvent subsystem, a co-solvent subsystem and a surfactant subsystem, comprises at least one monoalkyl branched propoxy sulfate anionic surfactant, where the microemulsion systems are useful in drilling, producing, remediation, and fracturing application to reduce water blocks and water blocking in formation of a production formation.

**LAVERGNE A., ZHU Y., PIZZINO A., MOLINIER V., AUBRY J. M.**
Synthesis and foaming properties of new anionic surfactants based on a renewable building block: Sodium dodecyl isosorbide sulfates.
*J. Colloid Interface Science* **360:** 645-653 (2011)
*ABSTRACT:* Two agro-based anionic surfactants containing an isosorbide moiety have been synthesized and their amphiphilic properties evaluated. Since isosorbide is now considered as an important platform chemical of the starch industry, these compounds could represent bio-sourced alternatives to the alkyl ether sulfates (notably lauryl ether sulfate, LES) that are based on petroleum-derived ethylene oxides. As isosorbide is an asymmetric diol, two isomers can be prepared (2-O-dodecyl isosorbide sulfate and 5-Ododecyl isosorbide sulfate) that show significantly different aqueous properties as regards to their Krafft temperatures and critical micellar concentrations. 5-O-dodecyl isosorbide sulfate is the most soluble and the most efficient surfactant. It possesses a much lower critical micelle concentration (cmc) than sodium dodecyl sulfate, SDS, leading to comparable foaming properties with a three times lower concentration. Its behavior compares well with the one of pure diethoxylated dodecyl sulfate that has also been prepared and evaluated in this work.

**KAKADJIAN S., ZAMORA F., GARZA T., MARQUEZ de SANTIS L., SALAGER J. L.**
Composition and methods for gas well treatment.
US Patent 7,989,404 B2 (August 1, 2011)
*ABSTRACT:* A microemulsion system is disclosed which comprises a solvent subsystem, a cosolvent subsystem and a surfactant subsystem which comprises at least one monoalkyl branched propoxy sulfate anionic surfactant, where the microemulsion system are usefull in drilling, producing, remediation, and fracturing application to reduce water blocks and water blocking in producing formation.

**SALAGER J. L.,**
La necesidad energética de petróleo en los próximos 20-30 años ¿Como seguir produciendo por nuevos métodos?
*5ta Convención de Ingeniería FUDESEV* (Petróleo y gerencia de hidrocarburos). Mérida 3-5/11/2011

**SALAGER J.L.**
Los hidratos de gas – Un potencial energético a futuro y un problema en la producción actual.
*3ras Jornadas Nacionales de Gas Natural*. Universidad de Los Andes, Mérida 17-19/2011

**BULLON J.**
La formulación : Una herramienta clave para la industria petrolera.
*Congreso de Ingeniería de Petróleo, Gas y Geológica*. *CPINPEG 2011*. Pedro Gonzalez, Margarita 12/11/20

**PEREIRA J.C., DELGADO J.G., SCORZZA C., RONDON M., SALAGER J.L.**
Breaking of water-in-crude emulsions. 4. Estimation of the demulsifier surfactant performance to destabilize the asphaltenes effect.
*Energy & Fuels* **25**: 1045-1050 (2011)
*ABSTRACT:* Surfactant molecules are tested as water-in-crude emulsion breakers to attain the quickest separation rate in the socalled "proportional regime". A concept of demulsifier performance is proposed on the basis of the required demulsifier concentration to offset the effect of a given amount of asphaltenes. The experimental evidence allows one to rank the tested products and relate their performance to their hydrophilicity and molecular weight. Some evidence indicates that the presence of acids in the crudemakes it easier to break emulsions and suggests that so-called "extended surfactants" can significantly shorten the demulsifying process.

**GALINDO-ALVAREZ J., SADTLER V., CHOPLIN L., SALAGER J.L.**
Viscous oil emulsification by catastrophic phase inversion: Influence of oil viscosity and process conditions.
*Industrial and Engineering Chemistry Research*. **50**: 5575-5583 (2011)
*ABSTRACT:* This study deals with the description of the influence of oil viscosity and process conditions on catastrophic phase inversion, through the analysis of the effects of formulation and process variables on the dispersed phase fraction at which the inversion is triggered. The in situ simultaneous follow-up of viscosity and conductivity measurements allowed, from a process point of view, to emphasize the effect of the aqueous phase addition rate on the catastrophic phase inversion point (PIP) and multiple w/O/W emulsion formation. Thus if the aqueous phase is added by very small fractions, formulation dominates and the inversion phenomenon can be accelerated, as a consequence of multiple emulsion formation, that greatly increases the volume of effective dispersed phase. An increase in oil viscosity greatly increased the tendency of the oily phase to become the dispersed phase and promoted the formation of highly concentrated emulsions (about 80 to 95% in volume) after inversion.

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