



Laboratorio de Formulación, Interfases,  
Reología y Procesos

<http://www.firp.ula.ve>  
Tel: +58 (0)274 240 2954 Fax: 240 2957



**2018 PUBLICATIONS AND SELECTED COMMUNICATIONS  
BY LAB. FIRP ASSOCIATES**

**PIERLOT C., ONTIVEROS J.F., ROYER M., CATTE M., SALAGER J.L.**

**Emulsification of viscous alkyd resin by catastrophic phase inversion with nonionic surfactant.**

*Colloids & Surfaces A*. **536**:113-124 (2018)

**ABSTRACT:** The addition of water to hydrophobic alkyd resin containing a hydrophilic nonionic surfactant (polyethoxylated-20-oleyl alcohol) was used to produce the emulsion morphology change from W/O to O/W in a small thermostated reactor (50 mL). The so-called catastrophic phase inversion of the water/alkyd resin system was detected by monitoring both, the viscosity by torque measurement and the electrical conductivity, until an equal weight fraction of water and resin is attained ( $fw = 0.5$ ). The two methods provide similar values of the phase inversion point (PIP). Although the determination of the PIP exhibits a small inaccuracy, it is clear that different torque profiles and PIP are observed depending on the resin neutralization level, the surfactant concentration and the water addition rate. For the non-neutralized resin, both, PIP and emulsion drop size, decrease with surfactant concentration increase. The completely neutralized resin could be emulsified using a minimum of 2 wt % of surfactant in the final emulsion. In such a case the water fraction at which inversion occurs ( $fw,Inv = 0.36$ ) is independent of the surfactant concentration and a small resin drop diameter ( $< 200$  nm) can be obtained. A more precise study of the reached drop size of the emulsion versus resin neutralization (0, 25, 50, 75, 100 and 125%) indicates that a minimum diameter is obtained around 90–100% neutralization, with no effect of overneutralization. For non-neutralized resin a maximum  $fw,Inv$  (0.25) can be obtained by reducing water addition rate allowing the production of 0.5  $\mu$ m droplets in a longer process.

**ONTIVEROS J.F., PIERLOT C., CATTE M., SALAGER J.L., AUBRY J.M.**

**Determining the Preferred Alkane Carbon Number (PACN) of nonionic surfactants using the PIT-slope method.** *Colloids & Surfaces A*, **536**: 30-37 (2018)

**ABSTRACT:** In this paper the Phase Inversion Temperature (PIT) of the  $C_{10}E_4/n$ -Octane/0.01M  $NaCl_{(aq)}$  emulsion was used as a reference to determine the changes introduced by adding small amounts of a second surfactant  $S_2$ . The so-called PIT-slope method allowed the calculation of the  $dPIT/dx_2$  value, i.e. the linear variation of PIT with the molar fraction  $x_2$  of second surfactant  $S_2$ . For nonionics polyethoxylated surfactants  $C_iE_j$ ,  $dPIT/dx_2$  showed a linear dependency respect to the Preferred Alkane Carbon Number (PACN), one of the parameters of the HLD equation based on phase behavior. We calculated here the PACN from PIT and  $x_2$  data for  $C_iE_j$  and other

nonionic surfactants derived from isosorbide or glycerol. When possible, the experimental PACN is determined from n-alkane scans at 25°C, and used to validate the proposed estimation method. The effects of changing the oil nature and water salinity on  $dPIT/dx_2$  are discussed in terms of the HLD equation and validates the hypothesis that allows calculate the PACN.

**ZAMORA J.M., MARQUEZ R., FORGIARINI A.M., LANGEVIN D., SALAGER J-L.**

**Interfacial rheology of low interfacial tension systems using a new oscillating spinning drop method.**

*Journal of Colloid and Interface Science* **519** : 27-37 (2018)

**ABSTRACT:** When surfactants adsorb at liquid interfaces, they not only decrease the surface tension, they confer rheological properties to the interfaces. There are two types of rheological parameters associated to interfacial layers: compression and shear. The elastic response is described by a storage modulus and the dissipation by a loss modulus or equivalently a surface viscosity. Various types of instruments are available for the measurements of these coefficients, the most common being oscillating pendant drops instruments and rheometers equipped with bicones. These instruments are applicable to systems with large enough interfacial tensions, typically above a few mN/m. We use a new type of instrument based on spinning drop oscillations, allowing to extend the interfacial rheology studies to low and ultralow interfacial tension systems. We present examples of measurements with systems of high and low tension, discuss the possible artifacts and demonstrate the capability of this new technique. We emphasize that the data shown for low interfacial tensions are the first reported in the literature. The instrument is potentially interesting in enhanced oil recovery or demulsification studies.

**SALAGER J-L., FORGIARINI A.M., MARQUEZ R.**

**Extended Surfactants: Origin, Distinctive Features, and Attractive Performances for Potential Applications.**

*Plenary Conference. 22<sup>nd</sup> International Symposium on Surfactants in Solution.* Norman OK USA, June 3-8, 2018

**ABSTRACT:** The published research in the past decades indicates that surfactant interfacial performance in producing low tension or high solubilization with polar oils is not attained with pure conventional surfactants exhibiting well defined polar and apolar portions. Introduction of the so-called extended surfactants, whose structure includes an intermediate polarity spacer between the head and tail groups. Recent investigations on different types and different applications such as detergency, cosmetics, enhanced oil recovery or crude demulsifying, indicate that these surfactants are likely to be particularly performing with problematical oils like high molecular weight paraffin, triglycerides or asphaltenic crudes. Emerging trends are analyzed to correlate the structure to the properties.

**MARQUEZ R., FORGIARINI A.M., FERNANDEZ J., LANGEVIN D., SALAGER J-L.**

**New interfacial rheology characteristics measured using a spinning drop rheometer at the optimum formulation of a simple surfactant-oil-water system.**

*J Surfactants & Detergents* **21**: 611-623 (2018)

**ABSTRACT:** A new spinning-drop tensiometer with an oscillating rotation velocity was used to measure the interfacial rheological properties of systems with very low interfacial tensions in the zone close to the so-called optimum formulation of surfactant-oil-water systems. 2 simple formulation scans were selected: One with an extended anionic surfactant using a salinity

variation in the water phase, and another with a mixture of 2 nonionic surfactants in a scan produced by changing their proportion. With both systems it was corroborated that at optimum formulation (i.e., at hydrophilic-lipophilic deviation (HLD) = 0), both the interfacial tension and the emulsion stability exhibit a deep minimum. A clear relationship was also found between the phase behavior and the interfacial rheological properties (dilatational elasticity and viscosity). For the very first time and in both kinds of scans (salinity or average ethylene oxide number), it was found that the interfacial elastic modulus  $E$  and the interfacial viscosity, as well as the phase angle also exhibit a minimum at optimum formulation. These groundbreaking findings could be applied to emulsion instability at optimum formulation and to its applications in breaking.

**MARQUEZ R., FORGIARINI A.M., LANGEVIN D., SALAGER J-L. I**

**On the instability of emulsions made with surfactant-oil-water systems at optimum formulation with ultralow interfacial tension.**

*Langmuir* **34** (31): 9252-9263 (2018)

**ABSTRACT:** We have studied emulsions made with two and three-phase oil-water-surfactant systems in which one of the phases is a microemulsion, the other phases being water or/and oil excess phases. Such systems have been extensively studied in the 70-80's for applications in enhanced oil recovery. It was found at that time that the emulsions became very unstable in the three-phase systems, but so far few explanations have been proposed. In the most complete one, Kabalnov and colleagues related the emulsion stability to the probability of hole nucleation in the liquid film separating two nearby emulsion drops, and associated this probability to the curvature elastic energy of the surfactant layer covering drop surfaces. We propose a different explanation, linked to another type of interfacial elastic energy, associated to compression of the surfactant layers. As found long ago, the three-phase systems are found near optimum formulation (Hydrophile Lipophile Difference  $HLD = 0$ ), where the interfacial tension exhibits a deep minimum. The determination of interfacial elastic properties in low interfacial tension systems is not straightforward. In our present work, we used a spinning drop tensiometer with an oscillating rotation velocity. We show that the interfacial compression elastic modulus and viscosity also exhibit a minimum at optimum formulation. We propose that this minimum is related to the acceleration of the surfactant exchanges between the interface, oil and water, near the optimum formulation. Furthermore, we find that the surfactant partitions close to equally between oil and water at the optimum, as in earlier studies. The interfacial tension gradients that slow down the thinning of liquid films between drops are reduced by surfactant exchanges between drops and interface, which are fast whatever the type of drop, oil or water; film thinning is therefore very rapid and emulsions are almost as unstable as in the absence of surfactant.

**BREGE J.J., PIETRANGELI G., McKELLAR A., QUINTERO L., FORGIARINI A.M., SALAGER J.L.**

**Fluid formulation for cleaning oil-based or synthetic oil-based mud filter cakes.**

*US Patent Application* by Baker Hughes Inc. (filed January 30, 2018) Publication date: June 7, 2018. see <https://patents.justia.com/inventor/jean-louis-salager>

**ABSTRACT:** A treatment composition may contact an oil-based mud (OBM) filter cake formed over the least part of a wellbore for incorporating more oil and/or filter cake particles into the treatment composition as compared to an otherwise identical composition. The treatment may include, but is not limited to, a surfactant, an aqueous based fluid, different acids and other agents like long chain alcohols, phenol derivatives, fatty esters.

**FORGIARINI A.M, SALAZAR F., and SALAGER J.L**

**Increasing Oil Recovery from Carbonates Using Chemical Pre-Flush Followed by Dilute Micellar Solutions.**

*SPE Workshop: Advances in EOR/IOR Technologies*, November 14-16, 2018. Manta, Ecuador

**ABSTRACT:** Carbonate reservoirs produce, typically, less than 10% OOIP during primary recovery, whereas waterflooding is effective in fractured reservoirs if the formation is water-wet. However, most fractured carbonate reservoirs are mixed-wet or oil-wet and oil recoveries are very low. In this work we study the influence of pre-flush in the recovery of crude oil from carbonates. For that, carbonate with light crude oil was aging at  $T = 120$  oC,  $P = 300$  Lbf/plg<sup>2</sup> by 48 hours. After that, the carbonate/crude matrix was pre-flushed with different aqueous solutions containing alcohols; polymers or surfactants before introducing a diluted micellar solution of LAS surfactant formulated at Winsor I and Winsor III type systems. Pre-flushes were carried out during 1-day at 120 oC, and the salinity of the systems was kept constant at 41,000 ppm (TDS). The spontaneous expulsion of oil was studied at Ph 7 and 9 during 10 days at 120 oC,  $P = 300$  Lbf/plg<sup>2</sup>. When brine was used as the soaking fluid, the oil recovery was in the range of 0 to 12% OOIP. Imbibition with LAS surfactant micellar solution without preflush resulted in an additional recovery of 5 to 10% OOIP. However, when the imbibition with LAS surfactant was preceded with the preflush, and depending on the chemical used, the recovery increased by 35% at pH 7 and 48% at pH 9. The high recovery of crude oil is discussed considering the change in wettability of the system and the phase behavior of the WI and WIII type systems. The systems are described as a function of the contact angle of carbonate-fluid and water-oil interfacial tensions. The crude-oil was quantified spectrophotometrically by dissolving the supernatant liquid phase, containing the recovered crude-oil, with an organic solvent.

**TOLOSA L., MARQUEZ R., RENNOLA L., SANDIA B.. BULLON J.**

**An overview of today's project-based learning and hiw it has been implemented in the Chemical Engineering School at University of the Andes.**

*Educación Química* **29** (4) 36-48 (2018)

Reference <http://revistas.unam.mx/index.php/req/article/view/64701/59123>

DOI: <http://dx.doi.org/10.22201/fq.18708404e.2018.4.64701>

**ABSTRACT:** This paper builds on a project-based engineering learning strategy called RAIS 'Reproducing an Innovation Environment in the Classroom' applied in courses in the Chemical Engineering curriculum at the Universidad de Los Andes (ULA). It follows a previous investigation where the practical implementation of RAIS strategy is presented (Marquez et al., 2016), and in this occasion the theoretical fundamentals of the RAIS strategy are outlined. Authors take the common project-based learning to a new level by directly involving the students in the common start-up company practice, where the final product to be formulated and manufactured is not a requirement from an external client, but comes from real entrepreneurship students' interests. In previous work it has been shown that this strategy allows interconnecting the course objectives with the development of a product. RAIS strategy has reported successful outcomes in the accomplishment of this goal for Chemical Engineering students at ULA.