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2016 PUBLICATIONS AND SELECTED COMMUNICATIONS BY LAB. FIRP ASSOCIATES

PIERLOT C., ONTIVEROS J.F., CATTE M., SALAGER J.L., AUBRY J.M.
Cone-plate rheometer as reactor and viscosity probe for the detection of transitional phase inversion of Brij30-isopropyl myristate-water model emulsion.
Industrial & Engineering Chemistry Research **55**: 3990-3999 (2016)
ABSTRACT: Brij30/isopropyl myristate/water model emulsions were used to study the inversion morphology change from O/W to W/O. The transitional phase inversion was detected by monitoring the electrical conductivity during a heating−cooling cycle while the viscosity of the emulsion was followed under constant shear rate with a cone−plate rheometer equipment. The two methods provide similar values of phase inversion temperature. However, different rheological profiles are observed depending on the surfactant concentration and water fraction. Viscosity maps of formulation-composition maps (specifically temperature−surfactant concentration and temperature−water fraction) pointed to the occurrence of both transitional and catastrophic inversion processes. A complete formulation−composition map with all different emulsion morphologies and isoviscosities contours for the 9% Brij30/IPM/water is presented. The use of a commercial cone−plate rheometer exhibits several advantages over the classical conductivity measurement; in particular, it does not imply any electrolyte addition in the aqueous phase and requires only a small volume of emulsion.

LATTES A., SALAGER J.L.
De la récupération assistée du pétrole a la renaissance en France de la chimie des tensioactifs.
In "*Histoire de la recherche contemporaine*", **tome V**, (1) 73-85. CNRS France (2016)
ABSTRACT: The first oil crisis was a sheer economic tsunami! In response, DGRST set up a committee to encourage researchers to study fundamental problems of Enhanced Oil Recovery, in particular by improved water injection. The many important results allowed an increase in the oil recovery rate and have made applications possible in various fields.

MARQUEZ R., BULLON J., FORGIARINI A.
Doble efecto de formulación producido por un alto porcentaje de alcohol en sistema Aceite/Dodecil Sulfato de Sodio/Pentanol/Agua y posible alteración del EACN del aceite.
Ciencia e Ingenieria **37** (2) 97-104 (2016)
ABSTRACT: **Dual formulation effect produced by a high content in alcohol in Oil/Sodium Dodecyl Sulfate/Pentanol/Water systems andresulting shift in oil EACN.** Triglyceride molecules are composed by three esters with three saturated or un-saturated hydrocarbon chains. Polar properties and low solubilization by conventional surfactants in microemulsions are

inherent to these types of oils due to their structure. In this work, the presence of a lipophilic alcohol (pentanol) influences the estimation of the Equivalent Alkane Carbon Number (EACN) of the oil in the the triglyceride oil-sodium dodecyl sulfate-pentanol-water system. Optimum formulation (HLD=0) was determined through formulation scans at the three-phase behavior or the minimum interfacial tension. It is observed that for coconut, corn, soybean and almond oils, the EACN obtained with a conventional anionic surfactant (sodium dodecyl sulfate) and a high percentage of pentanol is lower to those measured using extended surfactants. It is assumed that this deviation is due to a segregation of the pentanol in the oil phase, seggregated close to interface.

SALAGER J.L., FORGIARINI A.M., DELGADO J.G.
HLD optimum formulation as the main principle for breaking emulsions. Recents advances on the demulsifer performance in crude oil dewatering.
107th AOCS Annual Meeting, Salt Lake City, May 1-4 (2016)
ABSTRACT: Forty years ago a correlation between the characteristic physico-chemical variables of a surfactant-oil-water system was found as a numerical condition to attain a minimum interfacial tension in a formulation scan. Later, this so-called optimum formulation was also found to correspond to the most unstable emulsion. Many reasons were proposed to explain this coincidence, particularly the elimination of the Gibbs-Marangoni stabilization mechanism.
In the past decade new experimental techniques were developed and the attainement of an optimum formulation by producing an interfacial mixture of an added hydrophilic surfactant, called demulsifier, with the lipophilic natural surfactants present in crude oil (asphaltenes, resins, acids etc) was corroborated to be the main principle of crude oil dehydration. The so-called proportional regime condition allows to characterize the surfactant aspect of asphaltenes, which can be separated from their role as polar oil reducing the EACN. I also allows to compare the performance of different demulsifiers with different crude oils.
Secondary effects dealing with the self-association of asphaltenes, bulk and interfacial rheology, solvent-like and other additives may be dealt with at optimum formulation to make the emulsion even more unstable, i.e. to improve performance.

DELGADO-LINARES J.G., PEREIRA J.C,. RONDON M.J., BULLON J., SALAGER J.L.
Breaking a water-in-crude oil emulsion. 6. Estimating the demulsifier performance at optimum formulation from both the required dose and the attained instability.
Energy & Fuels **30** (7) 5483-5491 (2016)
ABSTRACT: Hydrophilic surfactant molecules with the proper formulation are able to break W/O emulsions stabilized by asphaltenes and other lipophilic amphiphiles as found in the effluent of petroleum wells. The demulsifier performance is here tested according to two critera. The first one, as in previous research, is the minimum dose of demulsifier used to attain the minimum stability at the so-called optimum formulation in a simplified bottle test. The second criterion is the value of this minimum stability at optimum formulation that has a direct relation with the separation time. Our findings show that, in a family of ethoxylated surfactants, the best demulsifier is a hydrophilic one, though not too much. When the demulsifier is a mixture of two surfactants, it usually exhibits an intermediate behavior between the components. However, the mixture sometimes appears to be better than any of the components alone with some synergistic effect that improves the performance.

SALAGER J.L., FORGIARINI A.M., BULLON J.

Predicting the interfacial tension change at optimum formulation in enhanced oil recovery.

Inform Magazine **26**: 14-19 (2016)

ABSTRACT: It has been clear since chemical enhanced oil recovery (CEOR) research began in 1974, that the most important issue in surfactant enhanced oil recovery (EOR) is the attainment of an ultralow interfacial tension between the oil and water fluids in the reservoir conditions.
Surfactant–oil–water systems were found to exhibit a low interfacial tension when the surfactant adsorbed at interface has exactly the same interacΘons with oil and water. This happens at the so-called optimum formulation, which corresponds to the minimum tension over a scan, the point at which a continuous change of a variable (like water salinity, oil and surfactant type, temperature) can alter the interactions between the adsorbed surfactant and the oil and water molecules.
The present article is a simplified version of a previously published report that addressed, for the first time, the quantification of the minimum tension versus formulation variables. The report received the 2014 American Cleaning Instutute's Distinguished Paper award at the 2015 AOCS Annual Meeting & Industry Showcases, May 3–6, in Orlando, Florida.
With a companion review paper on tension performance, the work reported here shows that it is now possible to predict the variation of minimum tension γ^* by appropriately changing two formulation variables.

DELGADO-LINARES J.G., ALVARADO J.G., VEJAR F., BULLON J., FORGIARINI A., SALAGER J.L.

Breaking of Water-in-Crude Oil Emulsions. 7. Demulsifier performance at optimum formulation for various extended surfactants structures.

Energy & Fuels **30** (9) 7065-7073 (2016)

ABSTRACT: The performance of several extended surfactants as water-in-crude oil emulsion breakers was evaluated using two criteria: (1) the demulsifier dose required (C_D*) to attain the minimum stability at the so-called optimum formulation, and (2) the corresponding low minimum stability value. These surfactants are found to behave in a similar way as typical commercial demulsifiers, i.e. they require a lower dose C_D* when their hydrophilicity is higher, but not extremely high. The reported data for a dozen of different extended surfactants indicate how the two performance indices are altered by changing the structure characteristics like the propylene oxide number PON, the ethylene oxide number EON and the ionic polar group (carboxylate, sulfate, phosphate). The actual best performance as demulsifier seems to depend on the proper combination of these structures to attain some well fitting compromise.

SALAGER J.L., FORGIARINI A.M., RONDON M..J.

How to Attain an Ultralow Interfacial Tension and a Three-Phase Behavior with a Surfactant Formulation for Enhanced Oil Recovery: A Review — Part 3. Practical Procedures to Optimize the Laboratory Research according to the Current State of the Art in Surfactant Mixing.

J Surfactants Detergents in press (2016)

ABSTRACT: The minimum interfacial tension to be reached in enhanced oil recovery by surfactant flooding implies the attainment of a so-called optimum formulation. Part 1 of the present review showed that this formulation may be described as a numerical correlation between the involved variables defining the oil, the water, the surfactant and the temperature. In

practice, the crude oil and connate water characteristics are defined for a given petroleum reservoir as well as by its temperature and pressure, so that reaching the optimum formulation requires a specific characteristic parameter of the surfactant used to satisfy the correlation. Since it is unlikely to find a single surfactant that would exactly match the crude/brine/T/P system characteristic of a reservoir, a mixture of at least two surfactant species is in general used. The scan technique method to test the mixing requires about 10 interfacial tension or phase behavior experiments and results in a single data. Hence, the scan experiments have to be repeated many times to find a minimum tension which is low enough. Part 2 of this review showed that there are many formulation variables and, consequently many posibilities to easily choose experimental conditions. Since there is no simple method to select two or more surfactant species, the choice is made from partial experience or intuition, and sometimes at random. The laboratory time and cost to reach an appropriate optimum formulation is often excesive. The present part 3 of the review shows that by cleverly selecting a three-surfactant mixture, the experimental work to attain a very low interfacial tension for a given reservoir case can be considerably reduced. The experimental strategy proposed here makes use of the available information along a proper step by step path toward the optimum.