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2019 PUBLICATIONS AND SELECTED COMMUNICATIONS BY LAB. FIRP ASSOCIATES

DELGADO-LINARES J., CARDENAS A. MORILLO N., GUEVARA M., BULLON J.
Asphaltene precipitation from Latin American heavy crude oils. Effects of solvent aromaticity and agitation on article size reduction.
J. Dispersion Science & Technology **40**:74-81 (2019)
ABSTRACT: Asphaltenes from three crudes were precipitated with a mixture of n-heptane and toluene, the size of the particles formed under different solvent mixtures and different agitation regimes were studied. The kinetic size reduction of aggregates formed with an excess of precipitant agent is fol-lowed, contrary to other published studies where the kinetic followed is of growing particles. It was found that the particle size of precipitated asphaltenes decreases as precipitant aromaticity increases and agitation energy rises, which indicates the formation of aggregates bonded by weak forces, since the agitation applied was not of high energy, except for the ultrasonic device.

MARQUEZ R., ANTON R., VEJAR F., SALAGER J.L., FORGIARINI A.M.
New Interfacial Rheology Characteristics Measured using a Spinning Drop Rheometer at the Optimum Formulation. Part 2. Surfactant–Oil–Water systems with a high volume of middle phase microemulsion.
J Surfactants & Detergents **22**:177-188 (2019)
ABSTRACT: This article is a continuation of our first study on dilational interfacial rheology properties at optimum for-mulation for surfactant-oil–water systems at low surfactant concentration just above the cμc. Here, we have investi-gated a high content of middle-phase microemulsion with an optimum WIII phase behavior for a system containing sodium dodecyl sulfate, n-pentanol, and kerosene. A new oscillating spinning drop interfacial rheometer was used to measure the interfacial properties. The very low dilational elasticity moduli and phase angle found at or near hydrophilic–lipophilic deviation (HLD) = 0 are related to the presence of the bicontinuous phase microemulsion and to the fast surfactant exchanges between the bulk and the interface, regardless of the phases involved in the measure-ment using the spinning drop apparatus, i.e., the two-phase excess oil and excess water (O-W) or the bicontinuous microemulsion and excess water (M-W). We show that at or near optimum formulation, the interfacial tension and the dilational modulus for the M-W case almost instantly reach equilibrium, because of the high surfactant content in the microemulsion and the fast exchanges

between the bulk and the interface. In contrast, when both excess phases (O-W) are measured, the changes in these properties are slower, due to the scarce presence of surfactants in both phases. The possibility of having almost all the surfactants trapped in the middle-phase bicontinuous microemulsion could explain the emulsion instability in all the WIII range. This is behaving as if there were no surfactant available in the oil and water phases to stabilize the oil or water droplets thus formed.

ALVARADO J.G., DELGADO-LINARES J.G., FORGIARINI A.M., SALAGER J.L.
Breaking of water-in-crude oil emulsions. 8. Demulsifier performance at optimum formulation is significantly improved by a small aromatic content in oil.
Energy & Fuels **33**:1928-1936 (2019)
ABSTRACT: Asphaltenes tend to aggregate in different structures depending on the aromatic content of the oil phase. The different aggregates adsorb at the interface as some kind of lipophilic surfactant, which tends to stabilize water-in-oil emulsions. Hydrophilic demulsifier molecules are added to combine with asphaltenes until the optimum formulation is attained at HLD = 0, thus resulting in the emulsion instability. It is found that with the change of asphaltenic aggregate structure produced by the aromatic content of the oil, its surfactant-like effect at the interface is also altered. The performance of dehydration is significantly improved with only 5% of aromatic additive in the oil phase.

FORGIARINI A., SALAGER J.L.
Optimization of EOR formulation using the well known simple HLD expression and recently understood tricks of surfactants nonlinear ternary mixtures.
SPE Workshop: EOR – The obligatory way to optimize mature fields, 29-30 May 2019, Mendoza, Argentina
ABSTRACT: For a given reservoir the oil EACN, the aqueous salinity, the temperature and pressure are given, and thus the surfactant characteristic parameter for optimum to be attained may be calculated from the HLD equation. For a binary mixture a composition scan between a hydrophilic surfactant and a lipophilic one produces an optimum with a tension minimum. For a ternary mixture of surfactants two binary mixtures produce two optimum formulations, whose blending exhibits an optimum optimorum, in general with a better performance. Non-linear mixing rules with interacting surfactants, as anionic, nonionic and extended, can produce better optimum zones not only with lower minimum interfacial tension, but also a wider region and thus robustness, as well as insensitivity to variations of salinity, temperature and surfactant mixture composition which can happen spontaneously in the process. Using the whole know-how allows to get a quick solution in practice without thousands of random trial and error experiments. Several cases of such events will be discussed: alkaline scans, anionic-nonionic and anionic-cationic mixture changes, linear change in composition in three-surfactant mixture, partial precipitation from a surfactant mixture in a salinity scan, and excessive partitioning of polyethoxylated nonionics.

SALAGER J.L., FORGIARINI A. M., MARQUEZ R.
Extended Surfactants including an alkoxylated central part intermediate producing a gradual polarity transition – A review of the Properties used in Applications such as Enhanced Oil Recovery and Polar Oil Solubilization in Microemulsions.

J Surfactants & Detergents **22**:935-972 (2019) DOI: 10.1002/jsde.12331
ABSTRACT: The research published in the past half century indicates that surfactant interfacial performance in producing low tension or high solubilization with polar oils is not generally attained with pure conventional species exhibiting well-defined polar and nonpolar parts. The improvement trends reached with surfactant mixtures as well as the introduction of additives like cosurfactants and linkers lead to the introduction of the so-called extended surfactants, whose structure includes an intermediate polarity spacer between the hydrophilic head and the lipophilic tail. Recent investigations on different kinds of surfactants in a variety of applications— such as detergency, cosmetics, enhanced oil recovery or crude demulsifying, and vegetable oil extraction— indicate that these extended surfactants are likely to be particularly performing with oils containing polar groups, such as triacylglycerols and asphaltenic crudes. Possible applications of extended surfactants in enhanced oil recovery, crude emulsion breaking, detergency and cleaning, medicine and cosmetics vehicles, and natural oil extraction as well as some other cases are quickly reviewed.

FORGIARINI A., BARRIO I., RODRIGUEZ B., AGUILAR F.
Control of asphaltene dispersion through the use of linear alkylbenzene sufonic acid.
Poster at the *11th World Surfactant Congress CESIO,* Munich Germany June 3-5, 2019
ABSTRACT: Results show that the dispersant power of LABSA increases with the molecular weight and it is a function of the dose added. Asphaltene dispersion was significant when acid concentrations were over 3% (p/v). It is concluded that the acids, mainly the LABSA 158, provide a good ability to disperse asphaltene molecules. The action mechanism of dispersants could involve the adsorption of LABSA on the asphaltene aggregates in order to generate a steric repulsion between them and to reduce the agglomeration and final precipitation, working as an inhibitor of asphaltene precipitation and at the same time as a dispersant.

FORGIARINI A., SALAGER J.L.
Optimization methods on surfactants mixtures to improve performance in EOR
Presented at the *40th* Annual IEA-*EOR*. *Cartagena de Indias, Colombia*. *September 16-20, 2019*
Enhanced Oil Recovery requires the attainment of ultra-low interfacial tension between crude oil and the injected aqueous phase. It is known that the lower the minimum tension is, the narrower the range of formulation over which it would take place. The objective of this work is to present the formulation strategies where the injected formula is as insensitive to changes in salinity, temperature or mixture of surfactant. This study allows to industry to understand how non-linear mixing rules with interacting surfactants, as anionic, nonionic and extended, can produce better optimum zones not only with lower minimum interfacial tension, but also a wider region and thus robustness, as well as insensitivity to variations of salinity, temperature and surfactant mixture composition which can happen spontaneously in the process. Using the whole know-how allows to get a quick solution in practice without thousands of random trial and error experiments.

MARQUEZ R., FORGIARINI A.M., LANGEVIN D., SALAGER J.L.
Breaking of Water-in-Crude oil Emulsions. Part 9: New interfacial rheology characteristics measured using a spinning drop rheometer at optimum formulation.
Energy & Fuels Asap (2019) DOI:10/1021/acs.energyfuels.9b01476

ABSTRACT: Water−crude oil interfaces often exhibit a viscoelastic layer with a high mechanical resistance, consisting of natural surfactants in crude oil, mainly asphaltenes, which stabilize water-in-oil emulsions. Shear and dilational interfacial rheological properties of these systems have been studied for more than 40 years. However, a clear understanding of the role of interfacial rheological behavior in water-in-oil emulsion destabilization at optimal formulation (when the hydrophilic lipophilic deviation, HLD = 0) has been established only a few months ago thanks to the use of an oscillatory spinning drop rheometer. In the first studies using this equipment, the dilational interfacial rheological properties of water−oil interfaces have been measured for very simple systems, with pure cyclohexane and pure surfactant, showing a very consistent new behavior. In the present work, different oils are used and the system complexity is increased up to be close to actual petroleum cases by including asphaltenes. As in systems without asphaltenes, a deep minimum in dilational modulus and phase angle is found at optimum formulation, thus showing that the reported interfacial rheology phenomenon is very general. Then, a practical approach for crude oil dehydration is designed, and the formulation scan is carried out by adding an increasing concentration of a surfactant acting as a demulsifier, as in the bottle test method usually used. For the first time with oil-containing asphaltenes, the occurrence of a deep minimum of interfacial dilational rheological properties is shown to happen at the point of minimum interfacial tension and maximum instability of emulsions, that is, at optimum formulation. This is a significant advance in the evaluation of the selected demulsifier performance for crude oil dehydration.

BULLON J., FORGIARINI A.M., SALAGER J.L., KOTEICH S., BAHSAS A., VIVAS J.A., MARQUEZ R., ROSALES Y.

Synthesis, Characterization, and Evaluation of Interfacial properties and Antibacterial activities of dicarboxylate anacardic acid derivatives from CNSL of Anacardium occidentale L.

Accepted *J Surfactants & Detergents* (2019)

ABSTRACT: Anacardic acid, extracted from cashew nut shell liquid (CNSL), has been structurally modified to obtain the 2-(O-carboxymethyl)-6-alkylbenzoic acid and its disodium carboxylate salt. Our separation method allows to easily obtain anacardic acid, which has been of interest for the fabrication of "green" products, due to its double functionality and the presence of saturated and unsaturated alkyl chain. These methods proposed for the first time to sinthesize these derivatives are short and cheap, and with a high yield. The elucidation of its structure was carried out by means of Infrared Spectroscopy (IR) and Nuclear Magnetic Resonance (NMR) techniques. Interfacial rheology properties of surfactant-air-water and surfactant-heptane-water systems were determined by using a new oscillating spinning drop rheometer apparatus. Physicochemical characterization was performed with a salinity scan in a surfactant-heptane-brine system, obtaining a value of the surfactant characteristic parameter σ = -4.6 for the disodium salt and a critical micellar concentration (cmc) of 0.08 wt%, showing high surface activity. The biological activity of both compounds was determined and measurements of their potential antimicrobial activity against Gram-positive and Gram-negative bacteria were performed, exhibiting high effectiveness, especially for the disodium salt against Gram-positive bacteria.