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2010 PUBLICATIONS AND COMMUNICATIONS BY LAB. FIRP ASSOCIATES

SCORZZA C., NIEVES J., VEJAR F., BULLON J.
Synthesis and physicochemical characterization of anionic surfactants derived from Cashew Nut Shell Oil.
J. Surfactants and Detergents **13**: 27-31 (2010)
ABSTRACT: Carboxylate derivatives of cardanol and anacardic acids, which are the main phenolic components of cashew nut shell oil are prepared and tested as anionic surfactants. They lower the surface tension, exhibit a critical micelle concentration, and produce microemulsions in mixtures with dodecyl sulfate. The value of their characteristic parameters in the hydrophilic lipophilic deviation (HLD) scale attained by the unidimensional formulation scan method typify them as hydrophilic surfactants.

VELASQUEZ J, SCORZZA C, VEJAR F, FORGIARINI A, ANTON RE, SALAGER JL
Effect of the temperature and other variables on the optimum formulation of anionic extended surfactants-alkane-brine systems.
J. Surfactants and Detergents **13**: 69-73 (2010)
ABSTRACT: Anionic extended surfactants of the alkyl polypropyleneoxide sulfate type are found to obey the linear correlation lnS = k ACN for optimum formulation (three-phase behavior) of ionic surfactant-oil-water systems, with a k value essentially the same as for n-alkyl sulfates. The addition of n-pentanol produces a shift in optimum formulation without significant change in k. An increase in temperature is found to produce a decrease in surfactant hydrophilicity, which is opposite to the expected behavior of anionic species. This trend, which reminds nonionic surfactant behavior, is probaby due to the partial hydration of the very first propyleneoxide units which are located close to the anionic head group.

ARANDIA M. A., FORGIARINI A. M., SALAGER J.L.
Resolving an enhanced oil recovery challenge: Optimum formulation of a surfactant-oil-water system made insensitive to dilution.
J. Surfactants Detergents **13**: 119-126 (2010)
ABSTRACT: Upon dilution by the petroleum reservoir connate water, the anionic commercial surfactant blend often used in enhanced oil recovery by low tension, becomes more lipophilic at interface because of the so-called selective partitioning. Hence, the optimum formulation is not maintained when the injected slug moves through the reservoir. An opposite variation is found for ethoyxylated nonionic surfactant systems. As a consequence of these antagonistic influences, the optimum formulation shift produced by dilution may be eliminated by using an appropriate mixture of anionic and nonionic commercial surfactants, so that the 2 effects exactly cancel out.

FORGIARINI A.M., SCORZZA C., VELASQUEZ J., ZAMBRANO E., SALAGER J.L.
Influence of the mixed propoxy/ethoxy spacer arrangement order and of the ionic head group nature on the adsorption and aggregation of extended surfactants.
J Surfactants and Detergents **13:** 451-458 (2010)
ABSTRACT: Two families of extended surfactants are prepared with the same head groups (carboxylate, sulfate, disodium phosphate) and different intermediate spacer structures. In one there are an average of 7 propylene oxide groups on the side of the tail and an average of 7 ethylene oxide groups on the side of the head, to produce a sequence of two different polarity segments. In the other case the spacer contains the same average numbers of propylene and ethylene oxide groups but in some homogeneous arrangement. The intermediate spacer structure without ionic head group, and in the cases of the carboxylate and sulfate extended surfactants, has a packing density reduction which is associated to the homogeneously alkoxide arrangement in the spacer. Such arrangement is found to produce about 20 % more surface area at interface, apparently because it results in some plumpness due to the spacer folding to remain close to interface. Both the critical micelle concentration and occupied interfacial area of the extended surfactant increase with the ionization of the anionic group associated to the electrostatic repulsion effect.

CELIS M.T., FORGIARINI A.M., MARQUEZ L., GARCIA-RUBIO L.H.
Characterization of nano-dispersions
Invited lecture - *Particles 2010*, Orlando FL USA, May 13-19, 2010
ABSTRACT: The result of any emulsification process, particularly the emulsion drop size, depends on many factors, particularly those related to the stirring protocol. However some emulsification processes, such as the so-called phase inversion method take place with minimum stirring, and produce the nanodispersions 20-500 nm range almost spontaneously, thus it has a considerable potential for practical applications, i.e., these fine emulsions may be used for encapsulation of oil-soluble bioactives, in skin care products and as colloidal drug carriers for pharmaceutical applications. The information contained in the UV-vis spectrum on scattering properties of the fine emulsions together with the optical properties of the dispersed phase lead to the interpretation of the spectra in terms of the droplet size and the distribution of this emulsificated systems. This research reports on a technique to monitoring the droplet size distribution of the nanoemulsions using spectroscopy. This particle characterization methodology is based on a sampling and dilution strategy combined with spectroscopy methods. It is shown that the sampling system integrated with a multiwavelength turbidity detector provides reliable information on droplet population. The spectra quantitative interpretation is performed in the spectral range (300 -820 nm) leading to reliable estimated of droplet size populations in the nanosize range. It is shown analyzes of nanoemulsions on transmission spectrum as a function of the oil concentration and the HLB value of the emulsifier, on the droplet size and distribution, and stability of the oil-in-water (O/W) emulsions attained by the phase inversion method.

AUBRY J.M., BOUTON F., CATTE M., DURAND M., MOLINIERV., NARDELLO-RATAJ V., PIZZINO A.
Le HLD, le EACN et les cartes formulation-cmposition: Trois outils concentuels pour la formulation des micro et des macroémulsions.
Journées sur les Emulsions, Bordeaux. May 2010

La construction et l'analyse physico-chimique et géométrique détaillée des diagrammes de phase de systèmes purement ternaires CiE4 / Hydrocarbure / Eau à différentes températures et pour différentes huiles (alcanes, alcènes, aromatiques, terpènes) nous ont permis d'expliquer l'influence de la structure chimique de l'huile sur la température de « fish » et de mettre en évidence certaines zones de diagrammes non explorées.
La comparaison des systèmes à l'équilibre avec les émulsions correspondantes obtenus par les processus d'inversion standard et dynamique souligne la relation étroite existant entre les diagrammes de phases et les cartes formulation – composition des émulsions

SALAGER J.L., FORGIARINI A.M., SCORZZA C., TOLOSA L.I., VELASQUEZ J., ACOSTA E.
Extended surfactants – A fine tuned structure to improve interfacial performance.
Presented in the *101th AOCS Annual Meeting,* Phoenix, May 16-19, 2010
ABSTRACT: Conventional surfactants exhibit well defined polar and apolar portions. The mixing of different surfactant species, as well as the introduction of additives like cosurfactants and linkers, allows to improve the performance as far as microemulsion solubilization and interfacial tension are concerned. However, such mixed components often fractionate, i.e., they partition between phases and interface in different ways; as a consequence, a hard-to-find optimum interfacial formulation is no longer insured when the surfactant concentration or water-oil ratio change, which is a very common occurrence in practice from laundry to enhanced oil recovery. Fastening together the mixture components in a single molecule that produces the same effect with no fractionation drawback, has been one of the goals of the so-called extended surfactant structure, which contains an intermediate polarity spacer between the head and tail groups. Recent investigations on different types and different applications such as detergency, cosmetics or crude demulsifying, indicate that these surfactants are likely to be particularly performant with problematical oils like high MW paraffin, triglycerides or asphaltenic crudes. Emerging trends are analyzed to correlate the structure to the properties and to guess about the next generation

SALAGER J.L., BULLON J., PIZZINO A., RONDON-GONZALEZ M., TOLOSA L.
Emulsion formulation engineering for the practitioner.
Encyclopedia of Surface and Colloid Science, **1**:1, 1-6. P. Somasundaran Ed., Taylor & Francis. (2010)
ABSTRACT: The formulation and formation of emulsions imply a very large number of variables, hence attaining the sought properties is usually long and tedious because of the large number of experiments to be carried out. The current state-of-the-art on physico-chemical formulation may be thoroughly used to considerably reduce the number of required experiments and to indicate to the formulator the relation between the kind of properties to expect and the generalized formulation expression. After this first order formulation factors selection is carried out, several second order factors are shown to be available to adjust the emulsion properties upward or downward in order to satisfy the specifications, either directly or by mean of a multistep process.

CELIS MT., FORGIARINI A., MARQUEZ L., GARCIA-RUBIO L.H.,
Influence of formulation on characterization of emulsions from transmission spectra.
Paper 129, *5th World Congress on Emulsion,* Lyon-France October 12-14, 2010.
ABSTRACT: An emulsion is a heterogeneous system containing two liquid phases, one of which

is fragmented in the form of droplets. The estimation of the droplet size and droplet size distribution is important data, not only because they are linked with the manufacturer process, but also they give valuable information on the properties of the liquid-liquid systems. The information contained in the UV-Vis spectrum on the scattering properties of the emulsions lead to the interpretation of the spectra in terms of the particle size distribution. The quantitative interpretation of the transmission spectrum is performed in the spectral range (300 -820 nm) leading to reliable estimated of droplet size populations in the range of 1- 20 μm as function of the oil concentration. The aims of this research is to demonstrate the potential of spectroscopy as a tool for characterization of emulsions in terms of droplet size and droplet size distribution, based in measurements of droplet populations as a function of oil concentration. These measurements are applied to emulsions originated of emulsifier/water/ monomer systems as a function of physicochemical variables, such as, nature and emulsifier concentration, and type of monomer. Results show the relation between formulation variables and properties of the emulsions from a single multiwavelength measured. It makes UV-Vis spectroscopy a powerful tool for characterization of dispersed systems.

DELGADO J.G., NOIK C., DALMAZZONE C., SALAGER J.L.

Electrical destabilization of petroleum emulsion.

Paper 206. *5th World Congress on Emulsion*, Lyon-France October 12-14, 2010.

ABSTRACT: The present study focused on the level of stability of emulsion formed with one crude oil containing at least 15% weight of surfactant material as asphaltenes. Asphaltene is the most polar part of molecules issued from oil precipitation, insoluble in aliphatic solvent. Gravity effect on emulsion stability was firstly analysed through classical bottle tests varying the dilution ratio of oil. Addition of cyclo-hexane solvent induces asphaltene aggregation and consequently modifies the interfacial properties. Relations between emulsion stability and interfacial tension are evidenced. Electrical stress is then studied using an electrical stability tester (EST) apparatus and determining the Critical Electrical Field (CEF). Tests performed on water-in-oil emulsion allow to follow the decrease of the critical voltage recorded at a fixed intensity which corresponds to the short-circuiting condition of the apparatus. Synergy is observed between electrical stress effect and action of added surfactant on the water droplet coalescence and consequently on emulsion destabilisation. Finally, direct observation of coalescence mechanism was performed through a microscopic visualisation on a dedicated cell where an electrical field is fixed. The droplets line up following the current intensity line was clearly evidenced before coalescence.

MARQUEZ L. COMPANY R., ONTIVEROS F., GONZALEZ J.C., NOBOA G., CELIS M.T., FORGIARINI A.

Effects of formulation on emulsion drop size in the vicinity of three phase behavior of surfactant-oil-water systems

Paper 061, *5th World Congress on Emulsion*, Lyon-France October 12-14, 2010.

ABSTRACT: Near the so-called optimum formulation (HLD = 0), approaching the Winsor III phase behavior, on one hand, the interfacial tension of surfactant-oil-water systems decreases, thus allowing the generation of smaller drops upon stirring; on the other hand, the coalescence rate increases, thus favoring the formation of larger drops. Both opposite effects acting together result in a minimum droplet size. Such a minimum drop size is found on both sides (for O/W and W/O emulsions) of optimum formulation, whatever the variable used to produce the scan. The

emulsion stability, and the location of these minima which correspond to the most efficient use of the stirring energy to make small droplets, depends on the formulation (change in HLD) and the alcohol molecule. Under certain formulation-agitation conditions, there is a first minimum for low interfacial tension regions and a second minimum for zones of high stability.

MARQUEZ R., FORGIARINI A., VEGA K., BRICEÑO M.I., MARQUEZ L., SALAGER J.L. Relationship between rheological behavior and the type of formed mesophase when preparing nanoemulsions.
Paper 153, *5th World Congress on Emulsion*, Lyon-France October 12-14, 2010.
ABSTRACT: Nanoemulsions are dispersed systems with a droplet size smaller than 100 nm. They are found in a wide range of applications, among them in cosmetics and pharmaceutical products. Their preparation requires the generation of a large interfacial area, which is attained by making use of the current know-how in physicochemical formulation of water/oil/surfactant systems. Water-Paraffin emulsions with Tween 80/Span 20 mixture at HLB = 12 and an initial oil-surfactant ratio of 75/25 were obtained by the Dilution Phase Inversion Method, which consists in adding water to the oil-surfactant mixture and then diluting the mesophase formed in water. The final emulsions contained 5 wt.% of the surfactant mixture, 15 wt.% paraffin oil and 80 wt.% of water. This preparation of nanoemulsions has been related to the formation of a liquid crystal phase during the water addition. Rheological behavior and conductivity of the formed mesophases were measured as well as the corresponding emulsion droplet size. These properties were monitored during mixing, beginning with the initial mesophase formation, in order to evaluate the time dependency of the emulsification process. Measurements of storage module G' and loss module G'' of mesophases composed by 10 to 40 % of water were related to the droplet size at the end of the emulsification process and the type of mesophase formed at equilibrium. A relationship was found between the non-equilibrium rheological behavior and the type of mesophase formed at equilibrium and its effect on emulsions droplet size, resulting from the equilibrium dynamics during nanoemulsification.

MERCADO R., SADTLER V., MARCHAL P., CHOPLIN L., SALAGER J.L.
Rheological study of the breaking of a cationic oil-in-water emulsion on Fontainebleau sandstone.
Paper 167. *5th World Congress on Emulsion*, Lyon-France October 12-14, 2010.
ABSTRACT: To optimize and control the road making processes, the physicochemical phenomena that occur during the breaking of a cationic oil-in-water emulsion by the addition of a negative-charged-surface solid are followed by rheological measurements. A model emulsion, with average droplet size of 15-20 microns, is prepared by dispersion of paraffin oil in cetylpyridinium chloride (CPC) aqueous solution. The results show that the oil fraction decreases after each addition of Fontainebleau's sandstone aliquots. As the droplets size and distribution remain constant during the process, we conclude that the emulsion heteroflocculation is the result of oil droplet adsorption on the sand surface, followed by the coalescence of the oil droplets around the sand particles.

FORGIARINI A., CELIS M.T, MARQUEZ L., SALAGER J.L.,
Properties of emulsions obtained with extended surfactants.
Paper 147. *5th World Congress on Emulsion*, Lyon-France October 12-14, 2010.
ABSTRACT: New extended nonionic surfactants, C12(PO)14(EO)n where n = 7, 12 and 20 were

investigated as stabilizers for n-alcanes/water and soybean-oil/water emulsions. These are nontoxic substances current investigations on different applications such as detergency, cosmetics or crude demulsifying, indicate that extended surfactants could be used to formulate micro or emulsion containing problematical oils like high MW paraffin, triglycerides or asphaltenic crudes. In this work was found that the droplet size of O/W emulsions depends on the ACN of n-paraffin as well as the hydrophilicity of the extended molecule, i.e when the extended surfactant was more hydrophilic, the minimum drop size was obtained for smaller values of ACN of n-alkanes. Extended surfactant formed soybean oil-in-water emulsion with small droplet sizes and high kinetic stability. Multiwavelength spectroscopy technique was applied for determination of the average diameter of the droplets.

FORGIARINI A.
Recuperación mejorada del petróleo. *4ta Convención de Ingeniería FUDESEV* (Petróleo y gerencia de hidrocarburos) Mérida 3-5/11/2010

SALAGER J.L.
Fluidos de perforación petrolera (lodos). *4ta Convención de Ingeniería FUDESEV* (Petróleo y gerencia de hidrocarburos) Mérida 3-5/11/2010

MERCADO R., SALAGER J.L., CELIS M.T., AVENDAÑO J.
Volumetría de determinación espectrofotométrica de un surfactante catiónico tipo diamina, mediante la formación de un complejo coloreado. [in Spanish]
Ciencia e Ingeniería **31** : 177-182 (2010)
ABSTRACT: **A Spectrophotometric Method to Determine a Cationic Surfactant of the Alkyl Propylen Diamine Type, via the Formation of a Colored Complex.** A simple, quick and accurate method is reported to quantitatively determine the concentration of a cationic surfactant of the alkyl propylen diamine type, which does not exhibit a chromophoric group and thus cannot be directly detected by photometry. Methyl orange is used as a chromogenic reagent to produce a derivative containing two methyl orange molecules per alkylamine molecule, that absorbs in the UV-Vis range. The absorbance variation versus the amine/methyl orange ratio allows the determination of the end point. Detection limits for alkyl amine range from 2x10-5 M to 3x10-4 M.

AGUILERA B.M., DELGADO J.G., CARDENAS A.L.
Water-in-oil stabilized by asphaltenes obtained from venezuelan crude oils.
J. Dispersion Science & Technology **31**: 359-363 (2010)
ABSTRACT: W/O emulsions were studied using asphaltenes as surfactants. Asphaltenes were obtained from three Venezuelan crude oils: ‘‘Lago Cinco,’’ ‘‘Rosa Mediano,’’ and ‘‘Ayacucho.’’ They were extracted using n-heptane as a precipitanting agent. The following variables were studied: concentration of asphaltenes in the oleic phase and pH of the aqueous phase. An increase in asphaltene concentration in the oleic phase increases emulsion stability. On the other hand, the most stable emulsions correspond to an alkaline aqueous phase. Likewise, emulsion stability was higher for asphaltenes obtained from ‘‘Lago Cinco’’ crude oil and lowest from Rosa Mediano asphaltenes.

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